Multi-Scale Simulation of Interfacial Phenomena and Nano-Particle Placement in Polymer Matrix Composites

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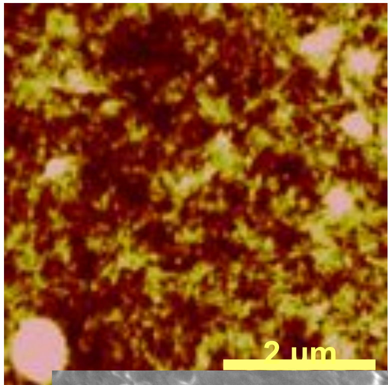
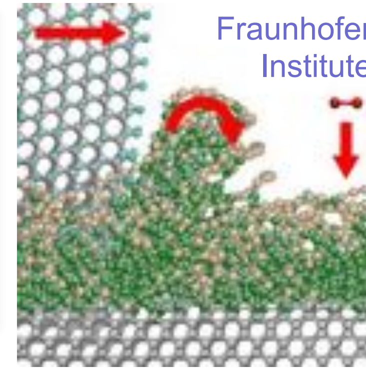
Interfaces: Cradle of Materials Functionality





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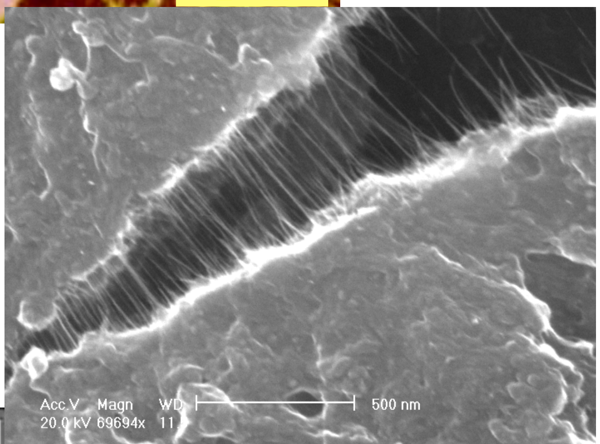
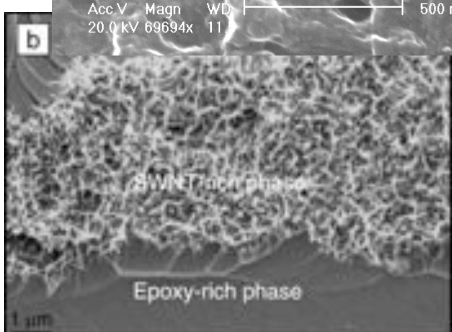
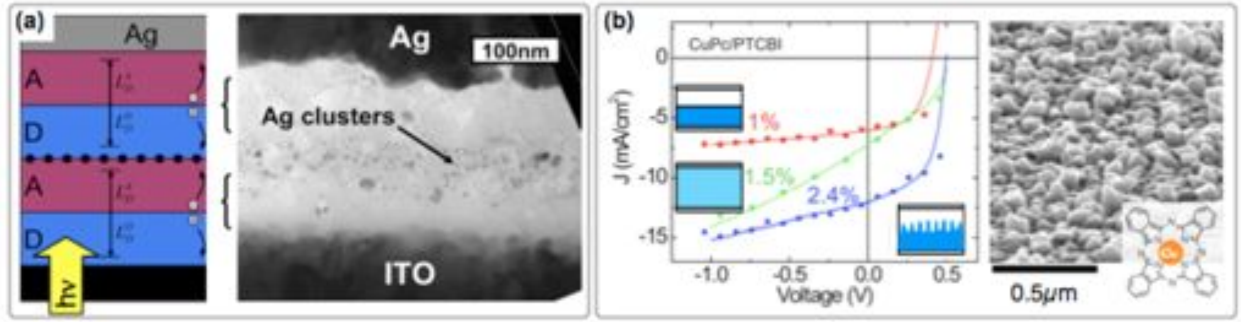
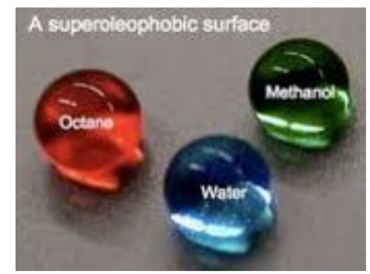




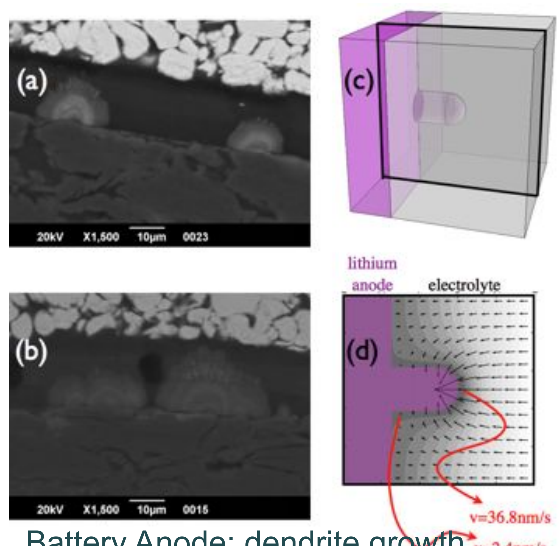
K.I. Winey, *et al.*, MRS Bulletin **32**, 348 (2007))



M. Shtein, pers. comm.

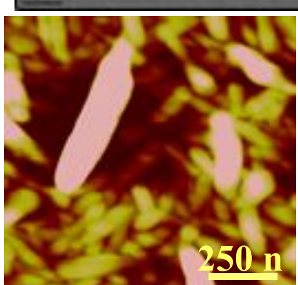


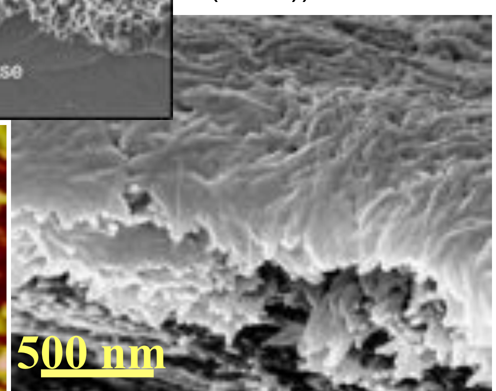
A. Tuteja, UM



Battery Anode: dendrite growth
E. Garcia, Purdue U.

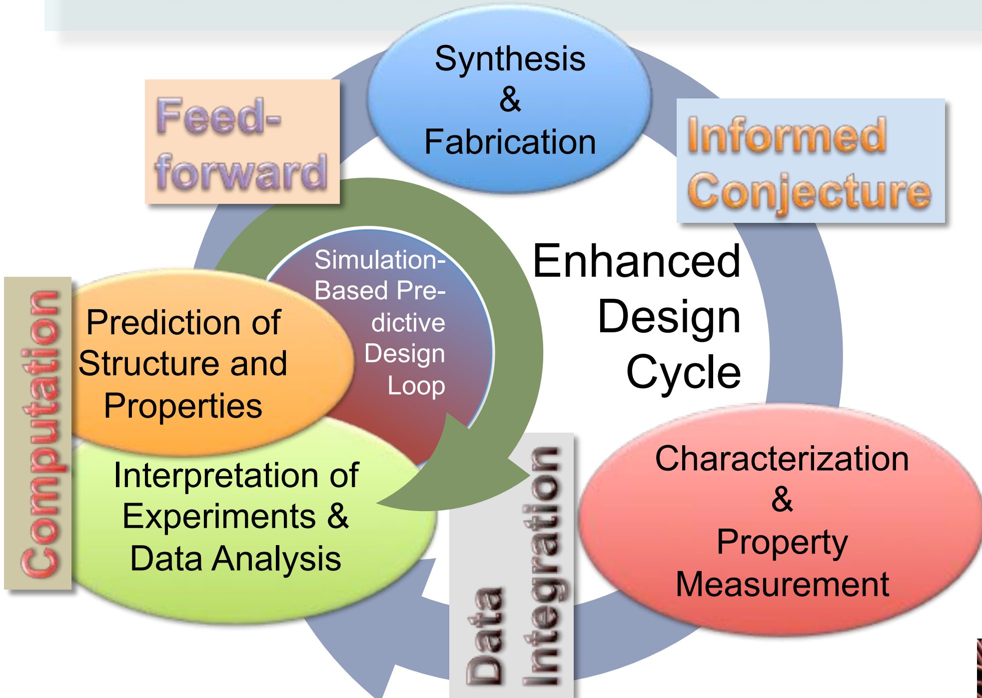
MEMS
Sandia National Labs



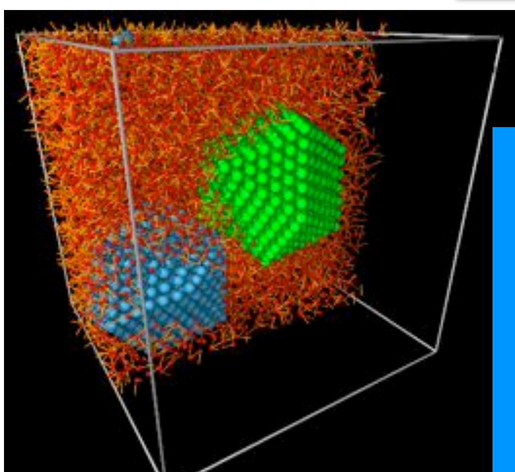


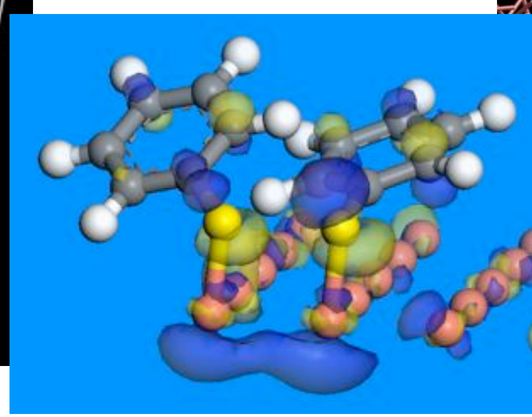
P. Podsiadlo *et al*. Biomacro. **6**, 2914 (2005)

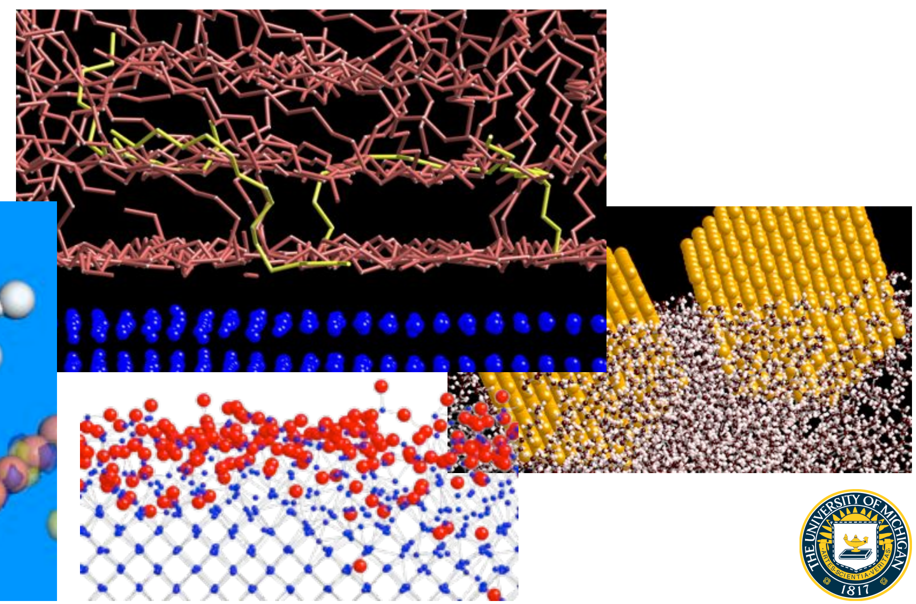
Simulation-Based Predictive Design



- Generate realistic structural models of interfacial regions by reproducing reactions and transport phenomena that underlie their formation
- Predict properties of these models
- Identify governing factors







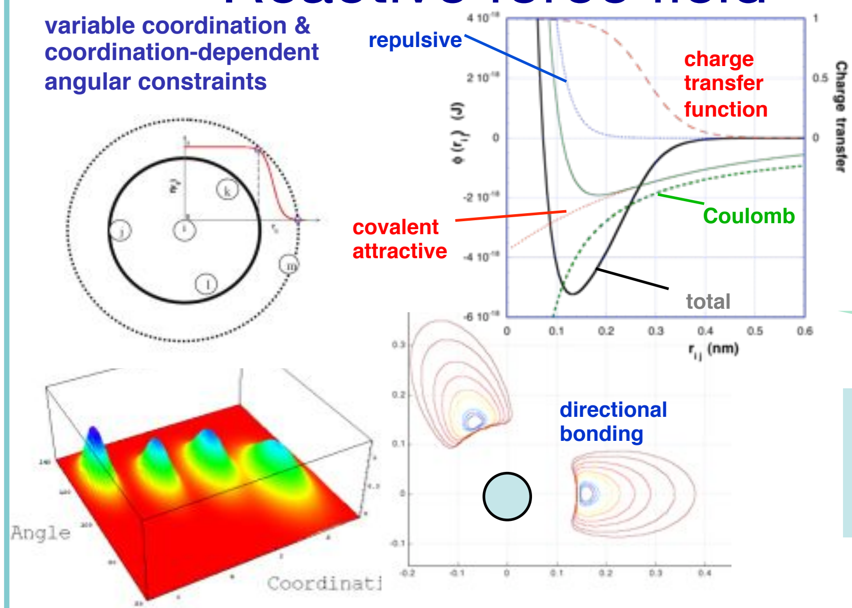
Outline

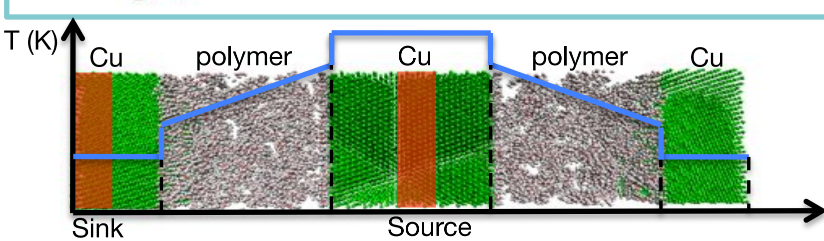
- ❑ Simulation Approach
  - ❖ Accurate force field models
- ❑ Generating Realistic Structures
  - ❖ Types of Structure Formation Processes
- ❑ Structural Ubiquities
  - ❖ Surface Patterning
  - ❖ Pronounced Layering
  - ❖ Densification of Polymer Near Interface
  - ❖ Formation of Gaps and Voids
- ❑ Property Prediction & Analysis of Governing Principles
  - ❖ Interfacial Strength Models
  - ❖ Thermal Boundary Resistance
- ❑ Summary and Outlook

Simulation Framework

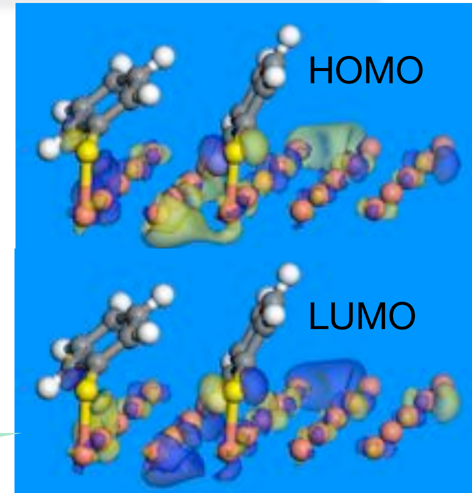
- ❑ Realistic structural models that account for nano-scale features are needed to predict interfacial properties
- ❑ Models generated using reactive molecular dynamics simulations
- ❑ Accurate description of atomic interaction models

Reactive force field



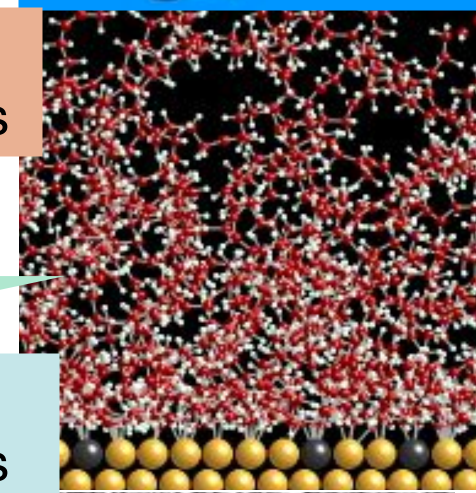


Density Functional Theory Calculations



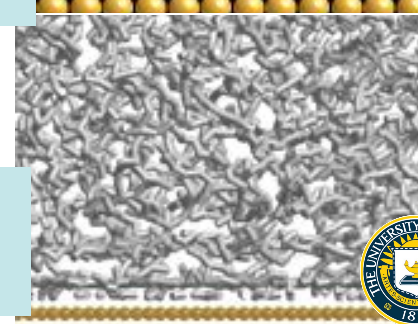
Local structure; Force field parameterization

Reactive Molecular Dynamics Simulations



Extended structure; Reaction Mechanisms; Predict Thermo-mechanical properties

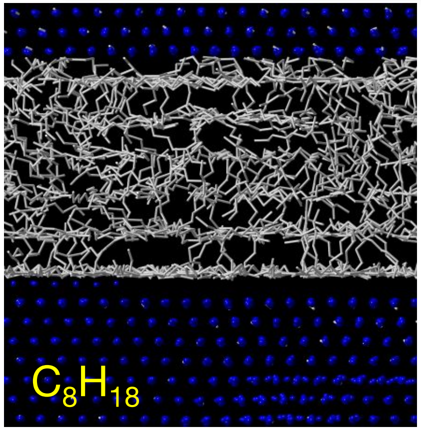
Coarse-Grain Particle Dynamics Simulations

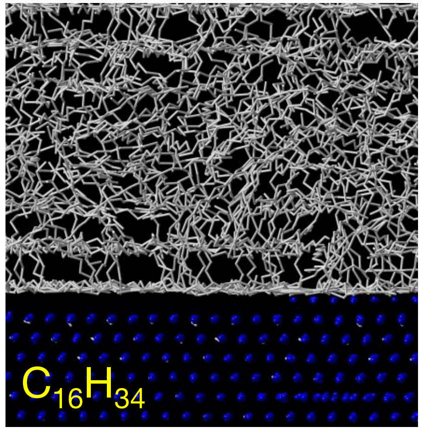


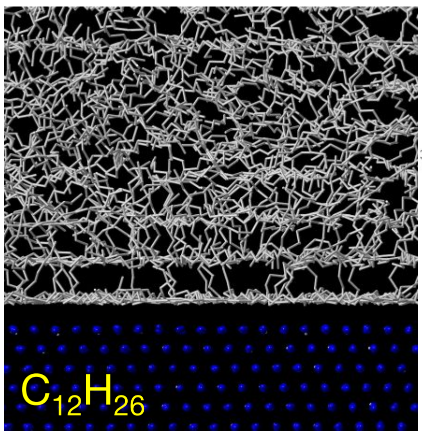
Accelerated simulation of structural evolution

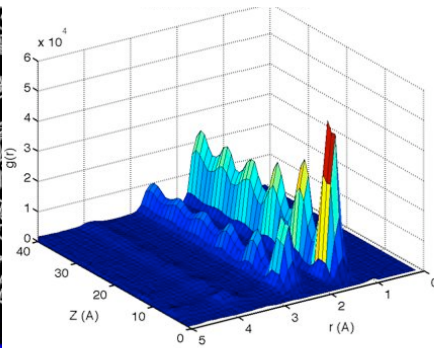
Validation, Verification and Interpretation

Generating Realistic Structural Models of Interfaces

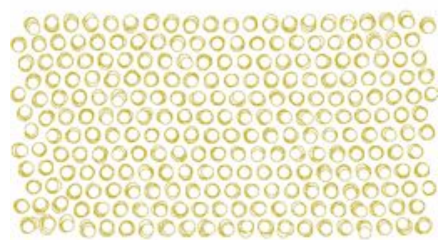




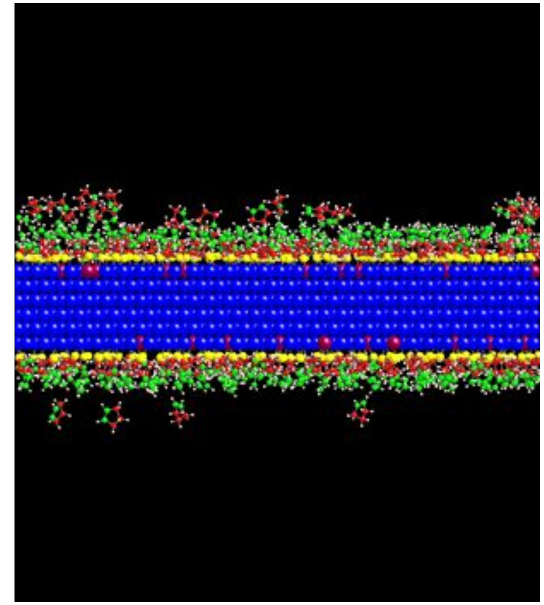




Vapor deposition

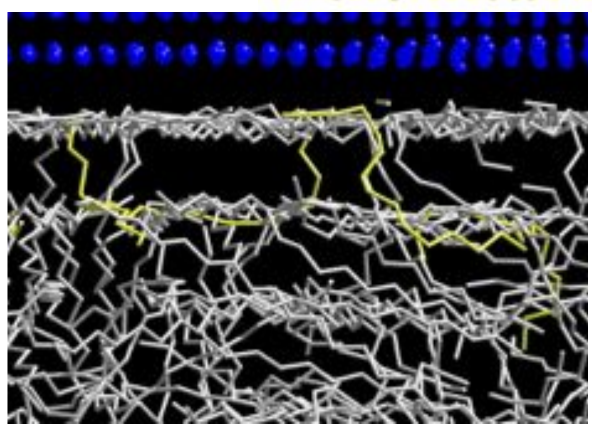


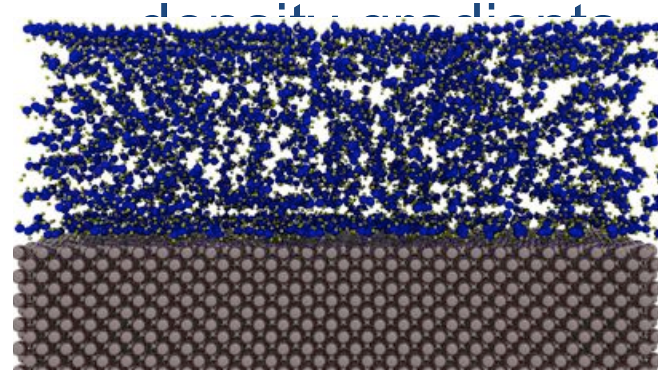
In situ polymerization



Adhesive forces can cause local

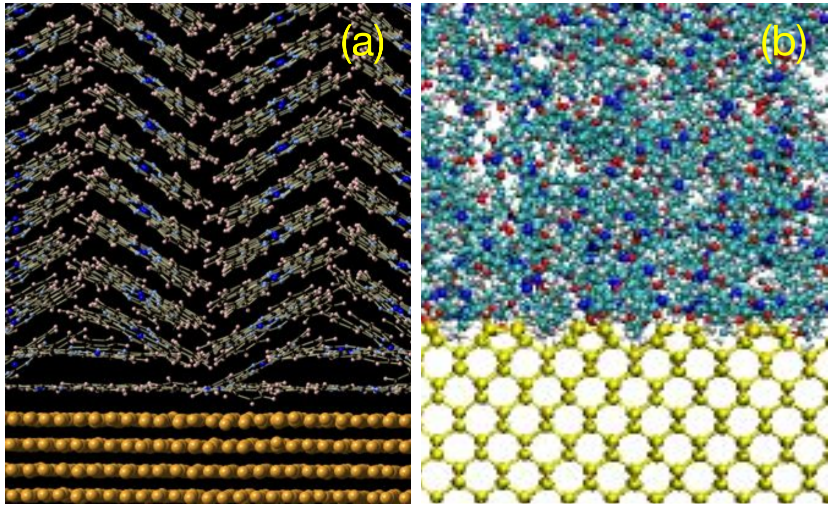
- ❖ Pronounced layering of polymer near interfaces affects mechanical properties
- ❖ Polymer chains span layers in “staircase” pattern



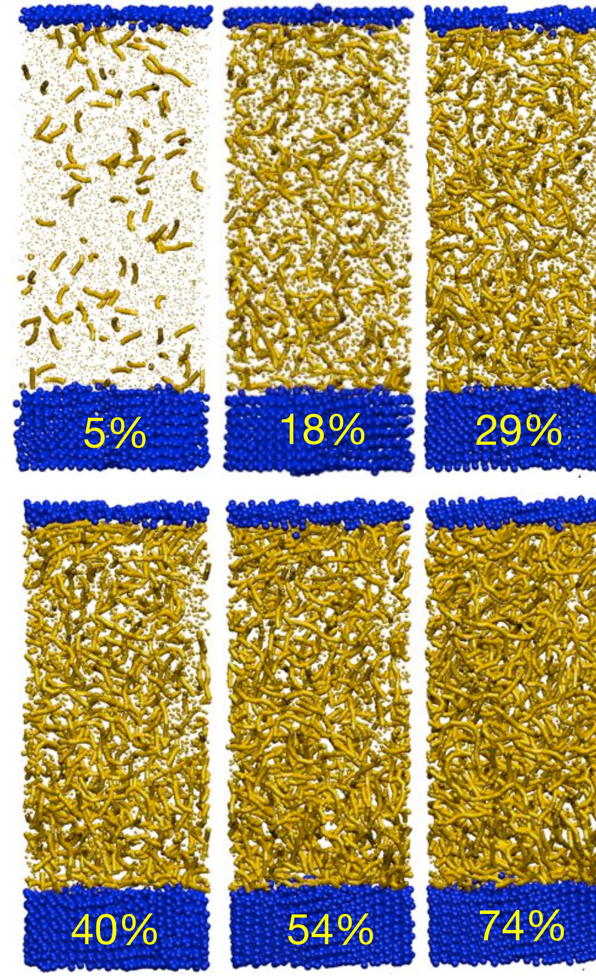


Generating Realistic Interfacial Structures

Three methods proved successful:
1. Juxtaposition of truncated bulk structures followed by relaxation
2. Simulation of the deposition process of thin layers
3. Simulation of the polymerization process near a substrate.

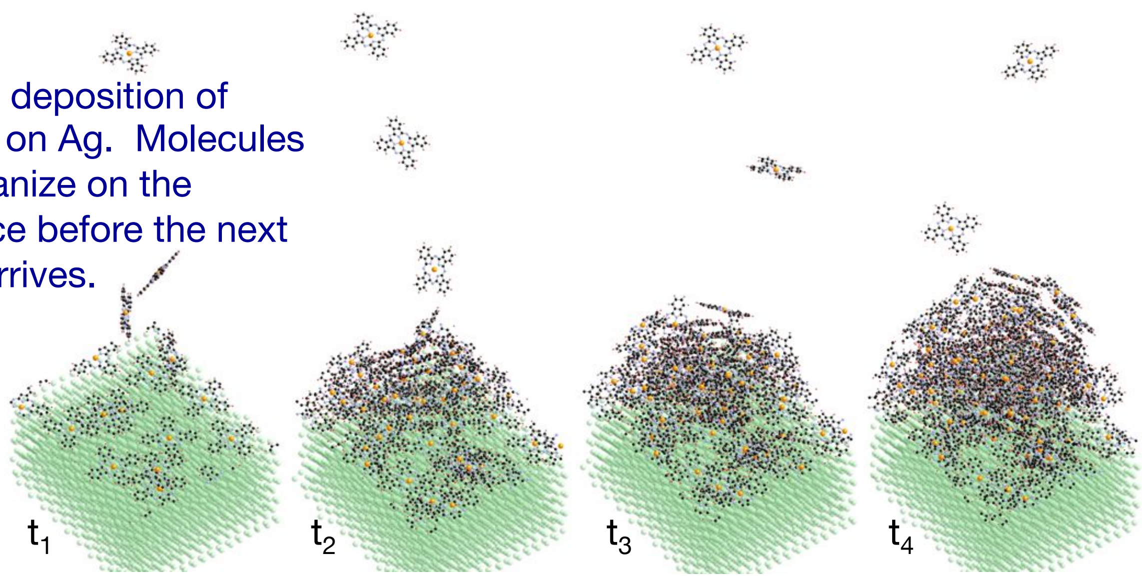


Interface between: (a) CuPc single crystal and Ag; (b) polyimide and Si obtained via phase juxtaposition

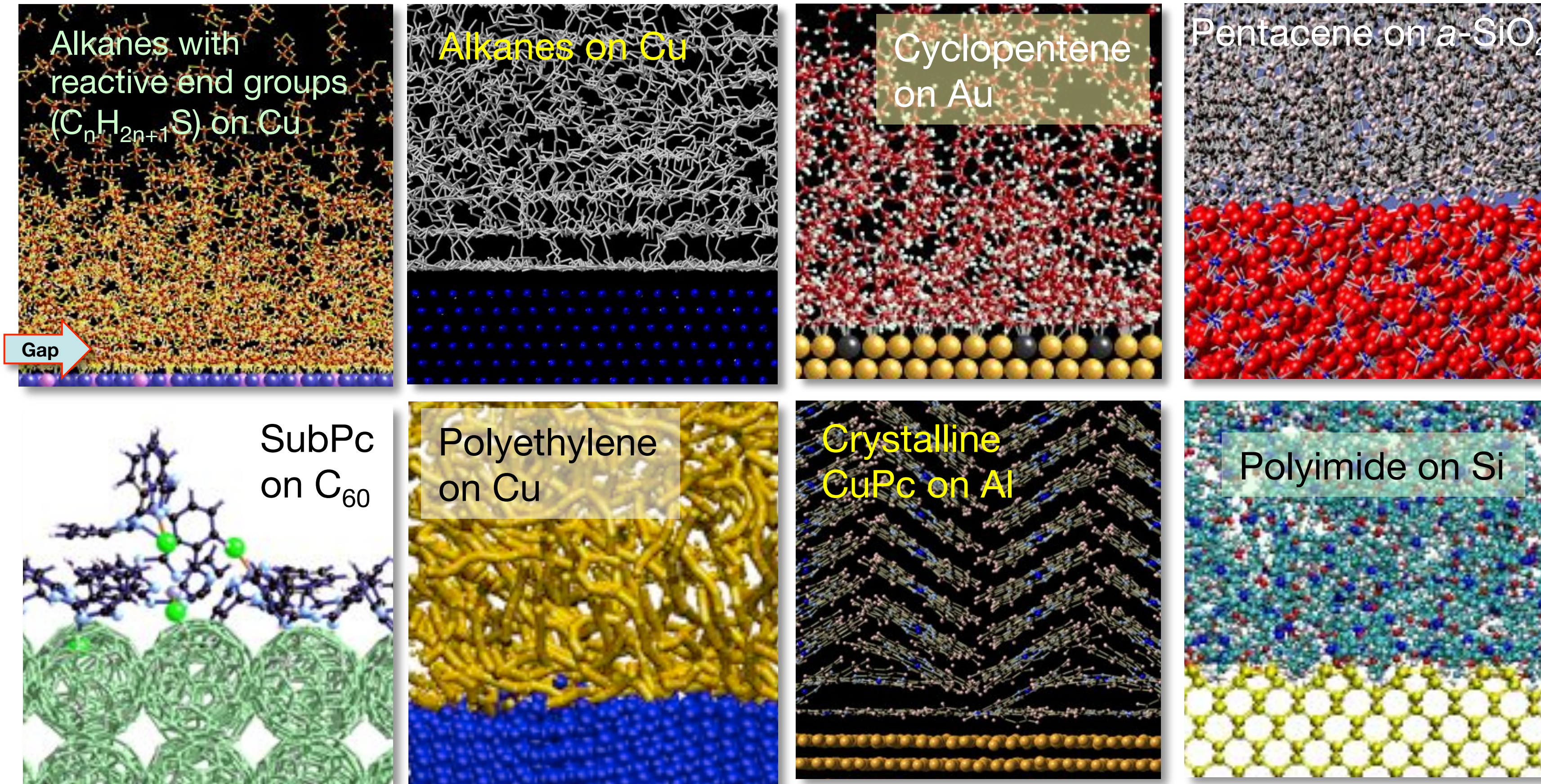


Polymerization of polyethylene in the gap between two Cu surfaces at various degrees of cure. Simulation involves a heuristic bonding scheme.

Vapor deposition of CuPc on Ag. Molecules reorganize on the surface before the next one arrives.



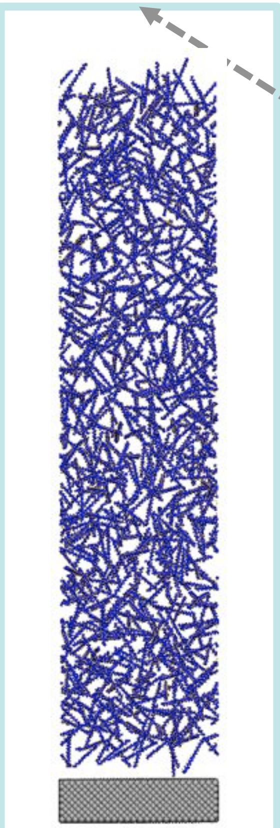
Materials Simulation Repertoire

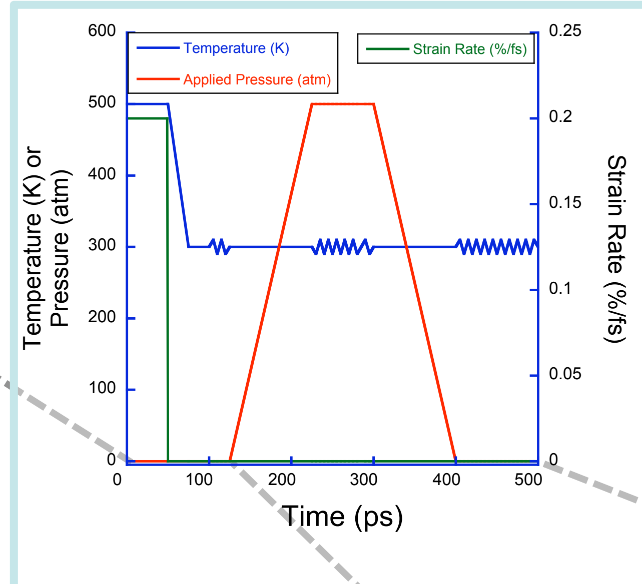


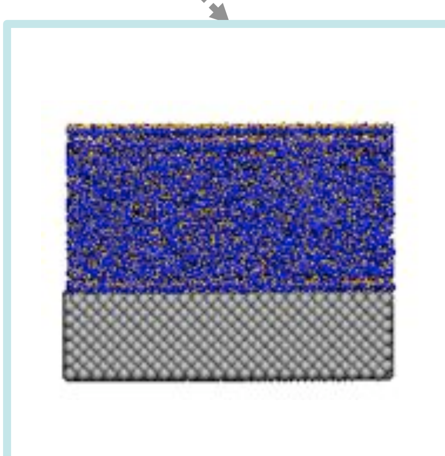
Systematic exploration of the chemical nature and structural complexity of interface systems

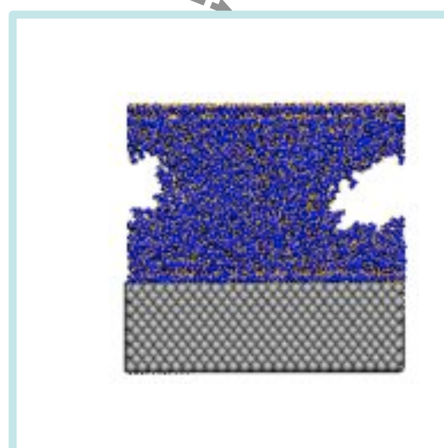
- Force field optimization based on the results from first-principles quantum mechanical calculations
- Development and verification of the structure generation strategy
- Property prediction and validation with known experimental data
- Structural analysis and identification of structure property correlations

Alkane/Metal: Simulation Details



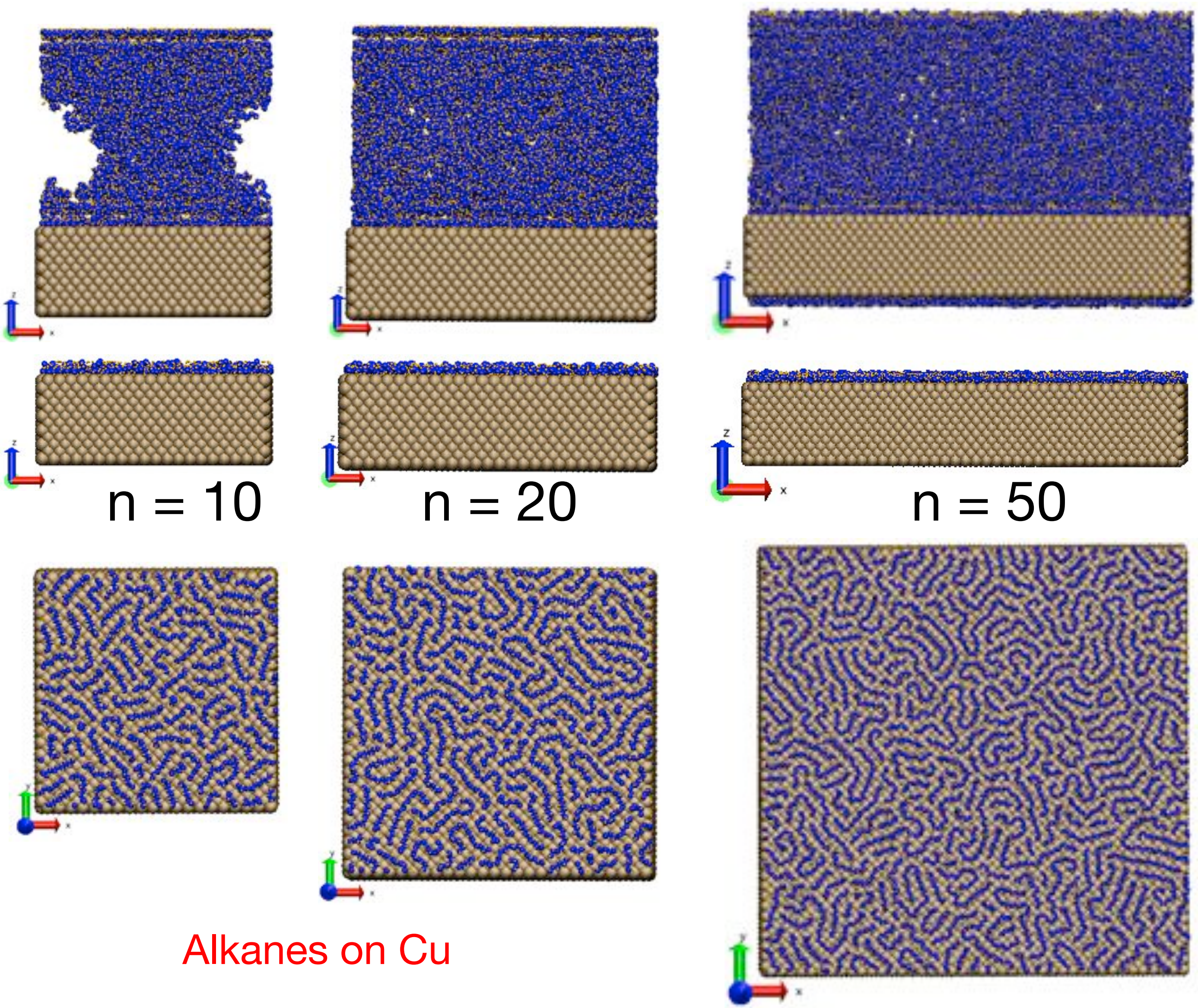






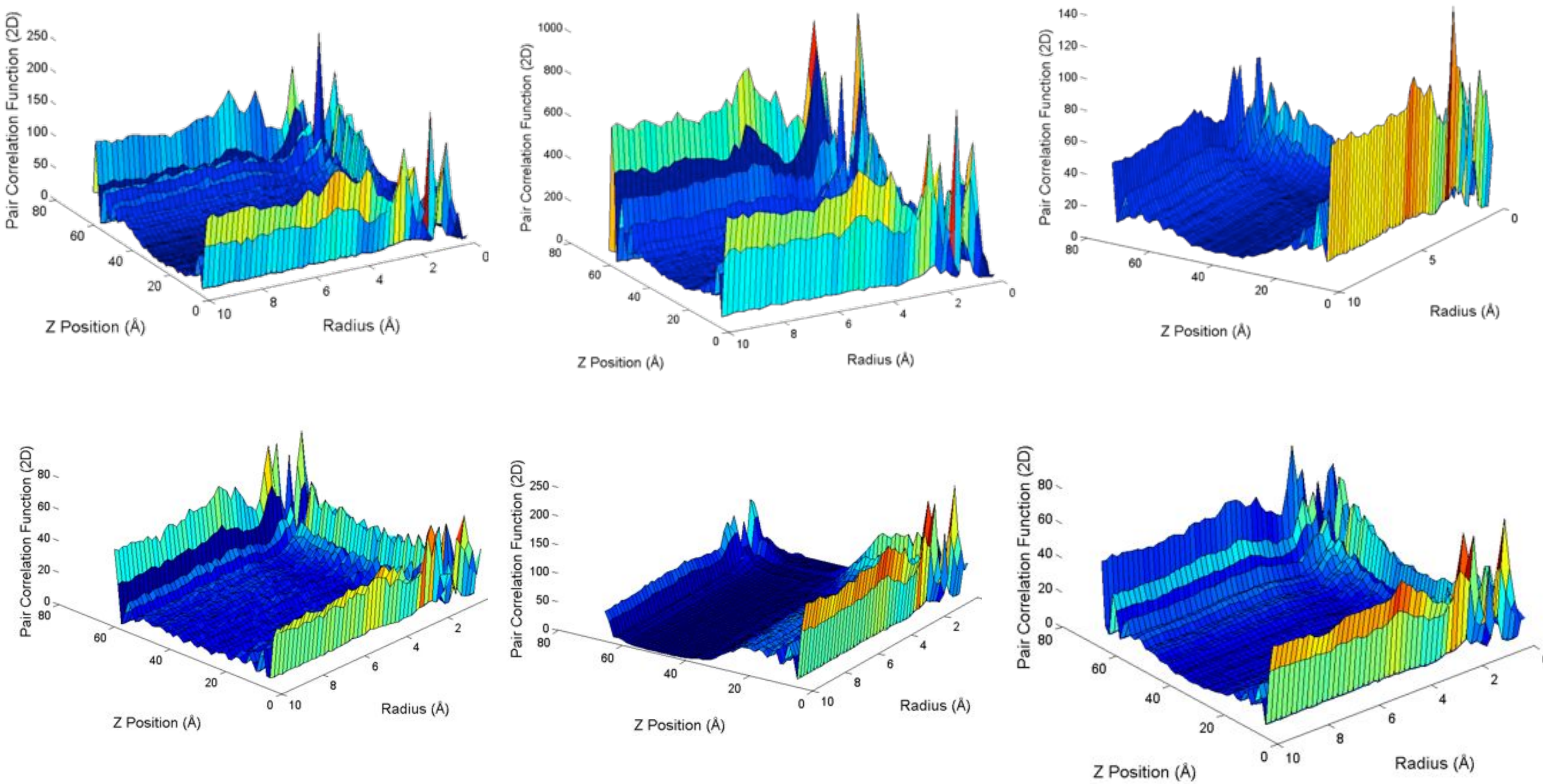
- ❑ Structure generated with random linear alkanes near fcc [100] surface
- ❑ Target thickness of 50 Å
- ❑ NPT phase required for structural stability

Surface Pattering – Chain Length



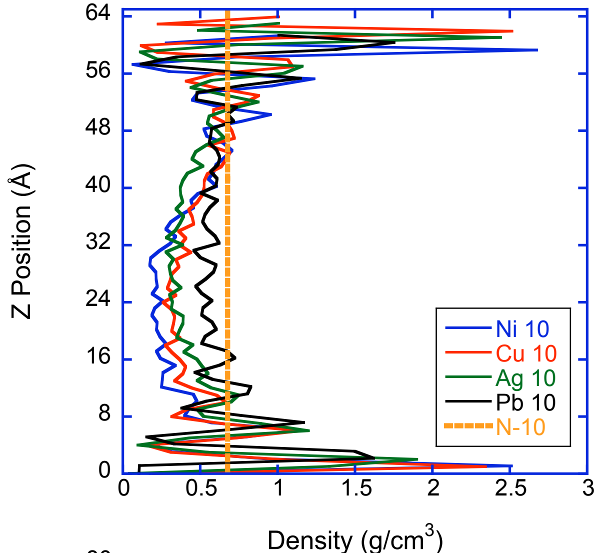
❖Alkanes of length *n*
❖Chain segments in direct surface contact are shown
❖Pattern no longer change appearance beyond threshold *n*

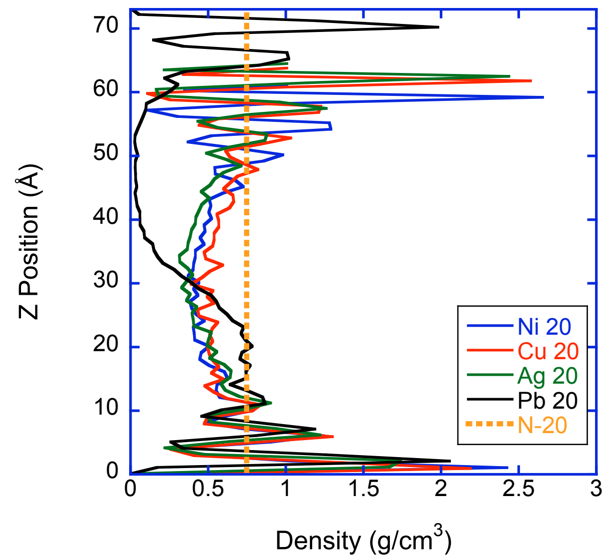
2D Pair Correlation Functions

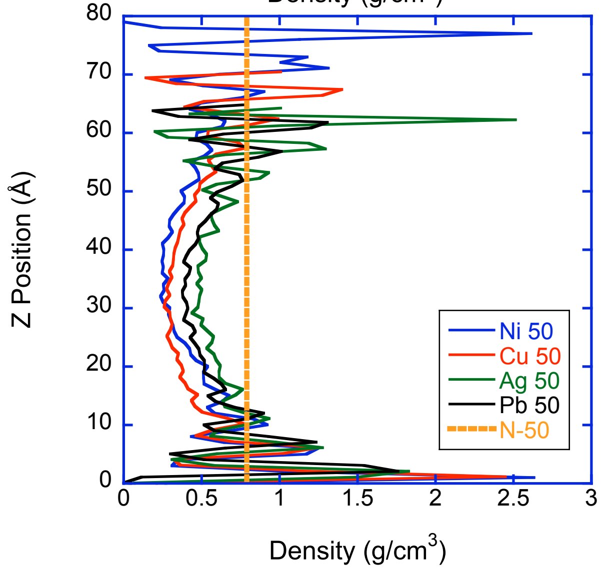


- Slice projected into 2 dimensions before pcf calculated
- Normalized according to overall average number density
- Upper: Nickel Lower: Lead Left to Right: n=10, n=20, n=50

Density Profiles Across Polymer Layer



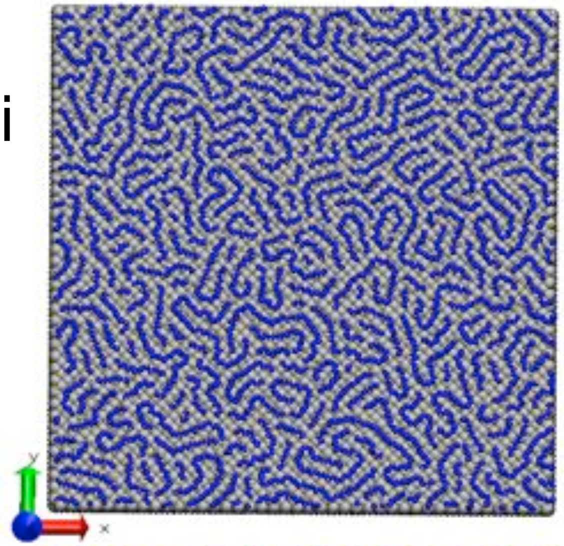




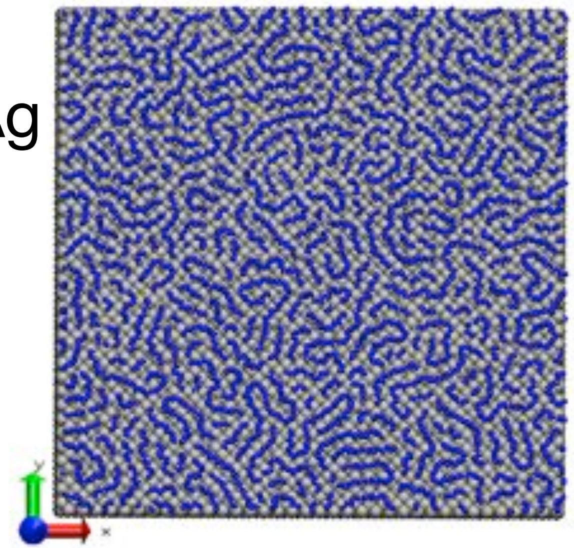
Voids present in the structures are reflected in the density profiles
Average density of bulk alkanes shown by dotted orange line

Surface Pattering – Substrate Lattice

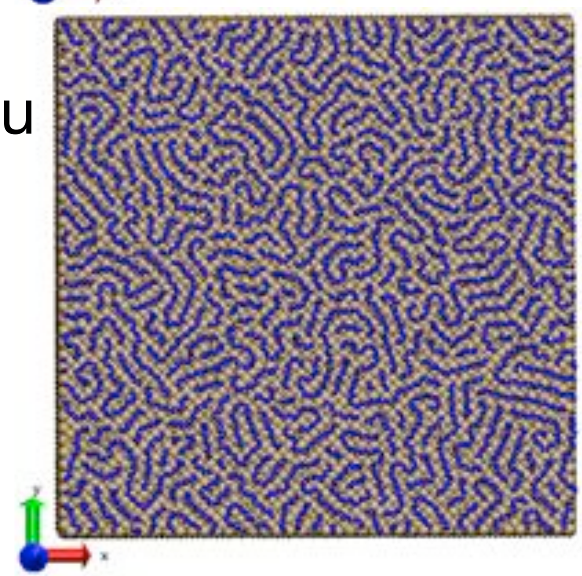
Ni



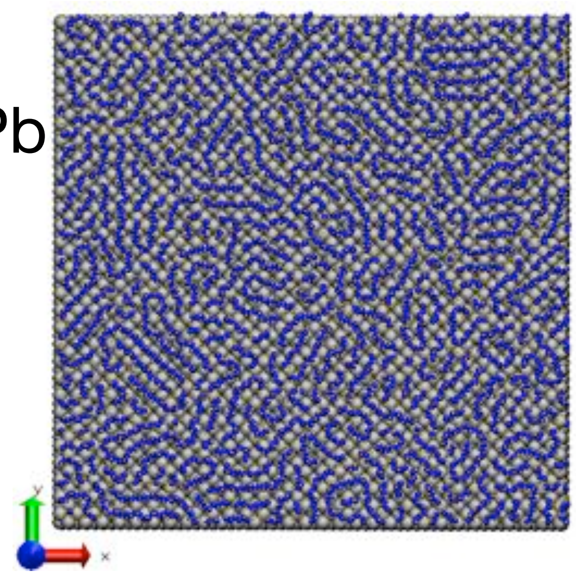
Ag

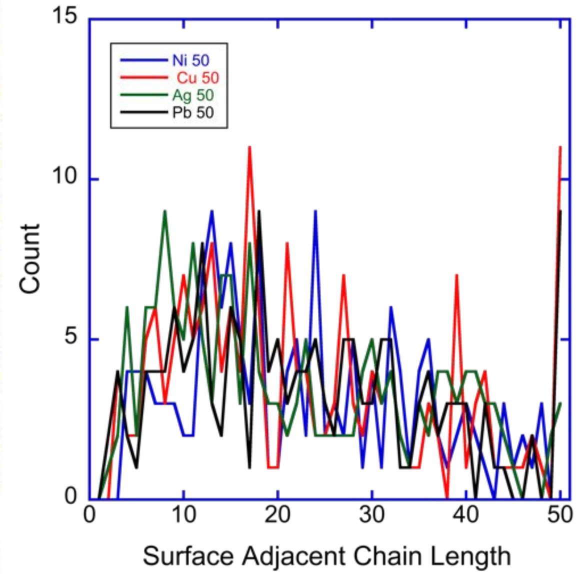


Cu



Pb

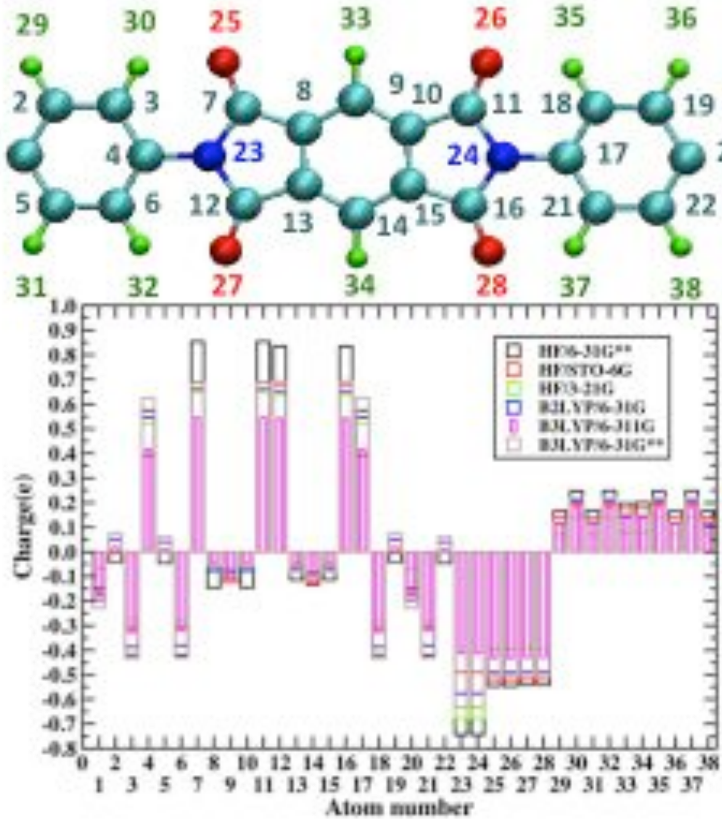


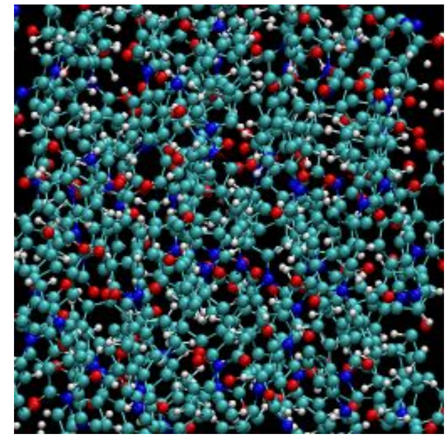


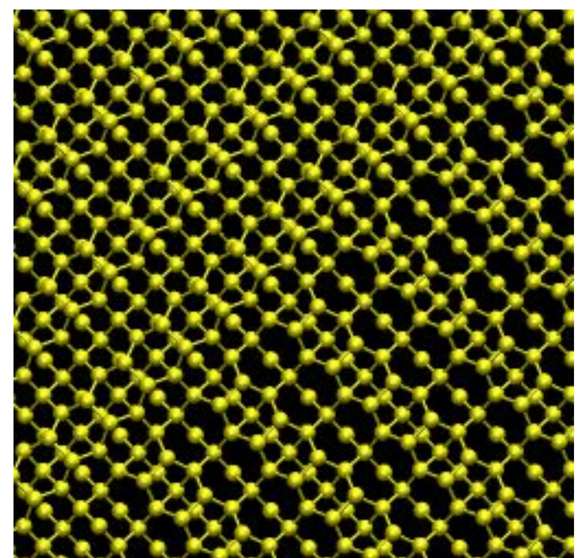
No apparent trend in surface patterns depending on substrate lattice parameters and interaction strentgth

Deposition of Polyimide on Si (100)

DFT optimized interaction potential for PMB molecule in bulk and with substrate

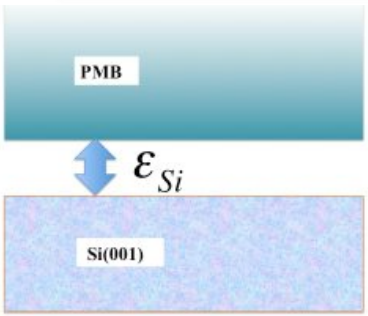






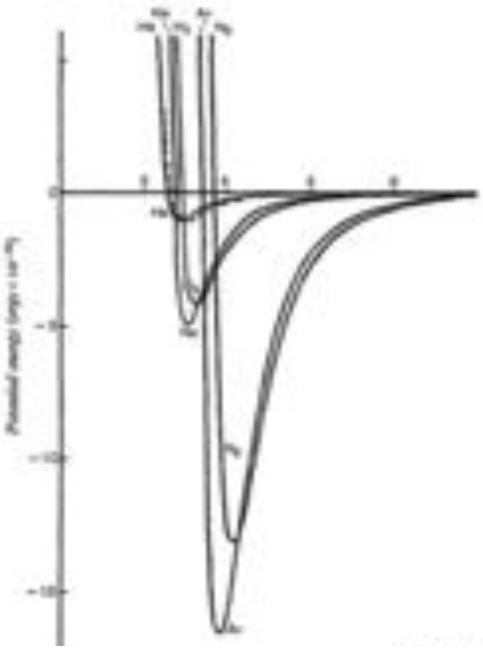
- **Silicon bulk and surface**
- **(2x1) dimer-reconstruction of the surface**
- **Surface steps on reconstructed surface**

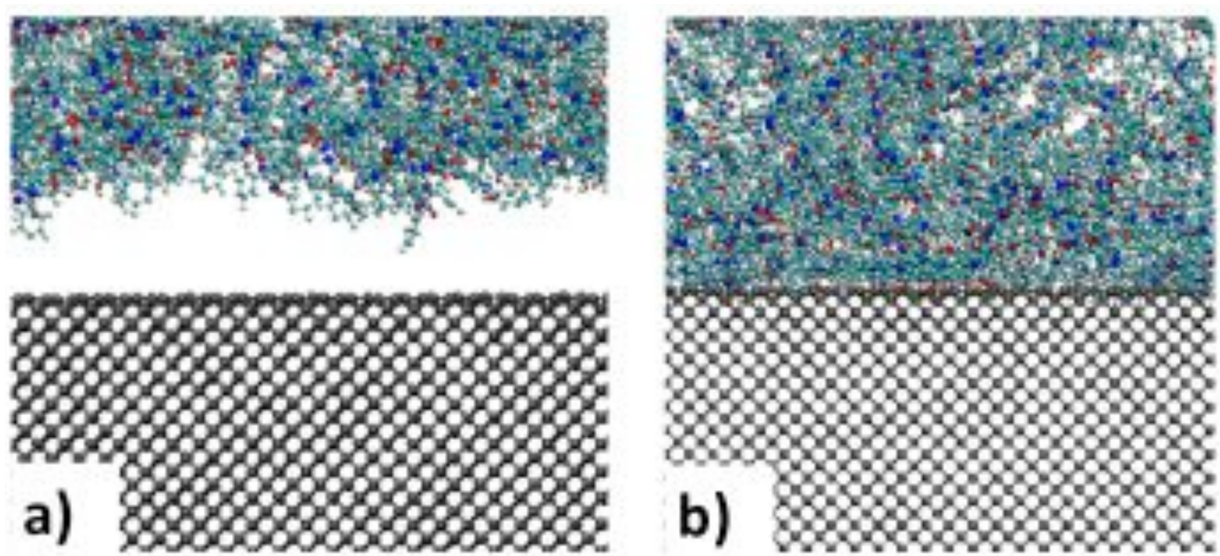
Polyimide on Si (100): Contact/ Non-Contact



Non-contact versus Contact Adhesion

a) Relaxation from a high-temperature state to a glassy state with under-critical interface coupling
b) Relaxation from a high-temperature state to a glassy state with interface coupling in excess of the critical



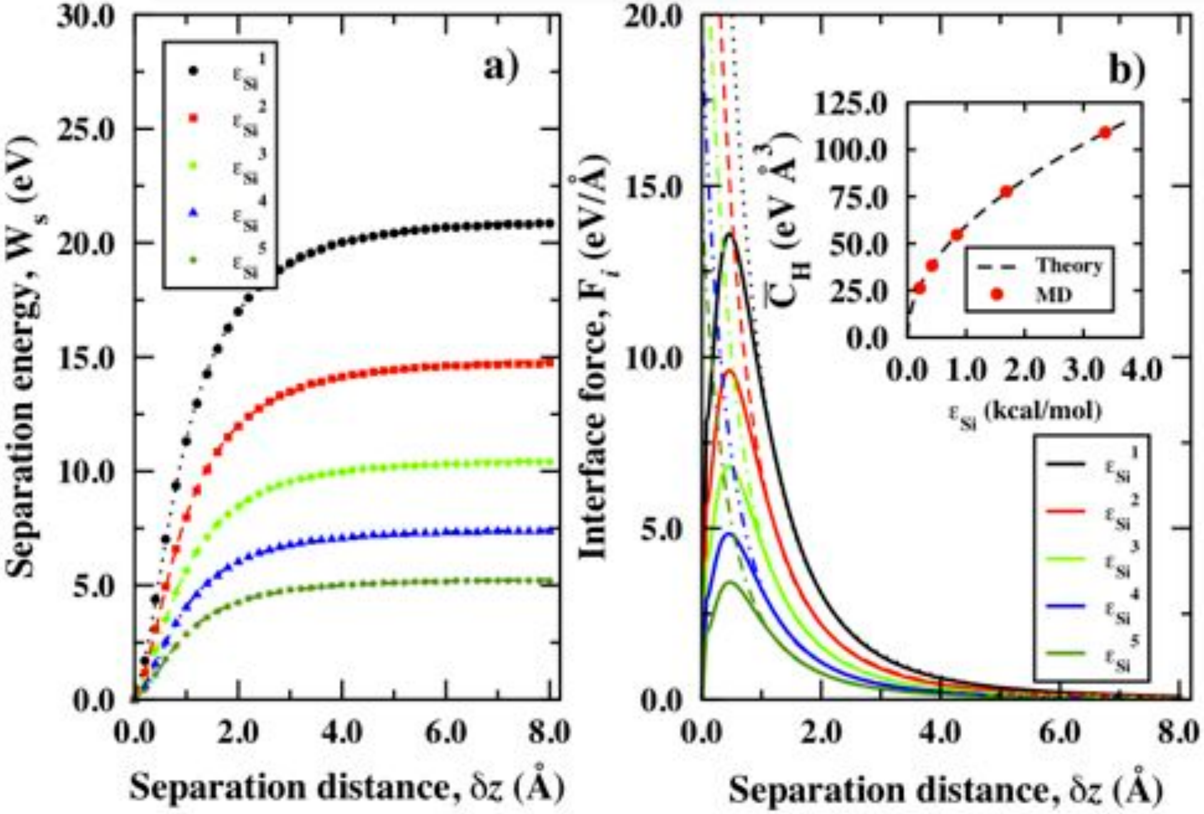


$$\varepsilon_{Si} < \varepsilon_{Si}^{c}$$

$$\varepsilon_{Si} > \varepsilon_{Si}^{c}$$

J. E. Lennard-Jones, “Cohesion”, Proc. Phys. Soc. 43, 461 (1931).

Energetics of PMB Layers on Si(001)



$$U^{R}_{Si-PI}(z_0) = 4\pi\varepsilon\rho_{Si}\left\{\frac{\sigma^{12}}{360}\left(\frac{1}{z_0^8} - \frac{1}{R_c^8}\right)\right\}$$

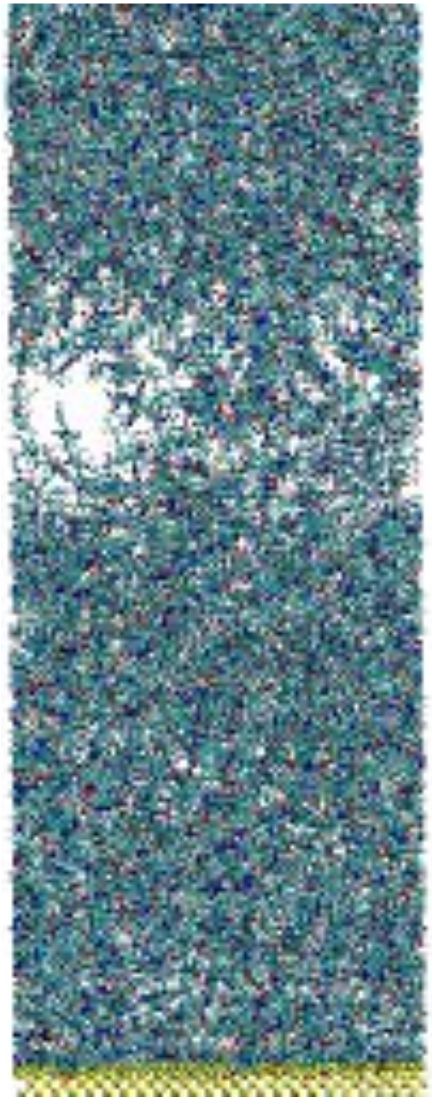
$$U^{A}_{Si-PI} = 4\pi\varepsilon\rho_{Si}\left\{\frac{\sigma^{6}}{12}\left(\frac{1}{z_0^2} - \frac{1}{R_c^2}\right)\right\}$$

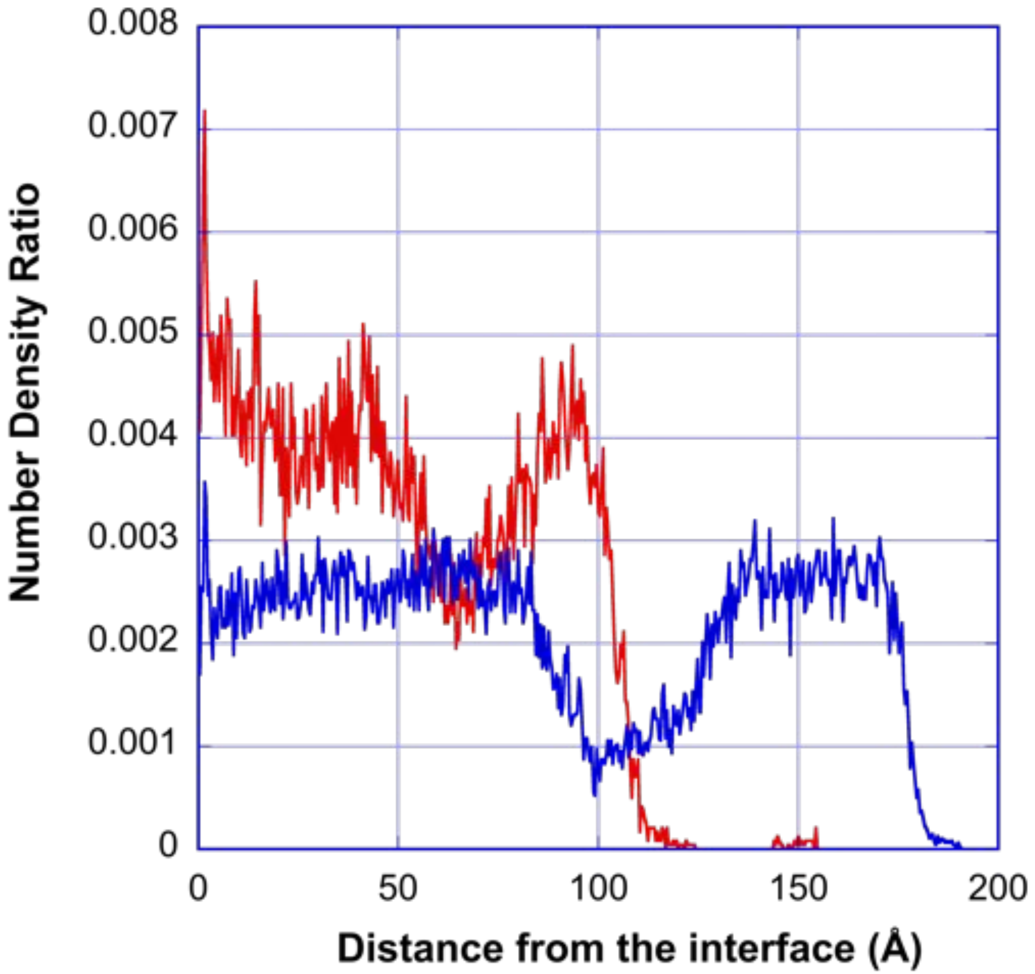
Simulated behavior (within the classical model of Si-PMB interfaces) is described well by the de Boer-Hamaker model with:

$$F_I = \frac{1}{24\pi}\left(\frac{3\pi C\rho_o\rho_{Si}}{z_0^3}\right)$$

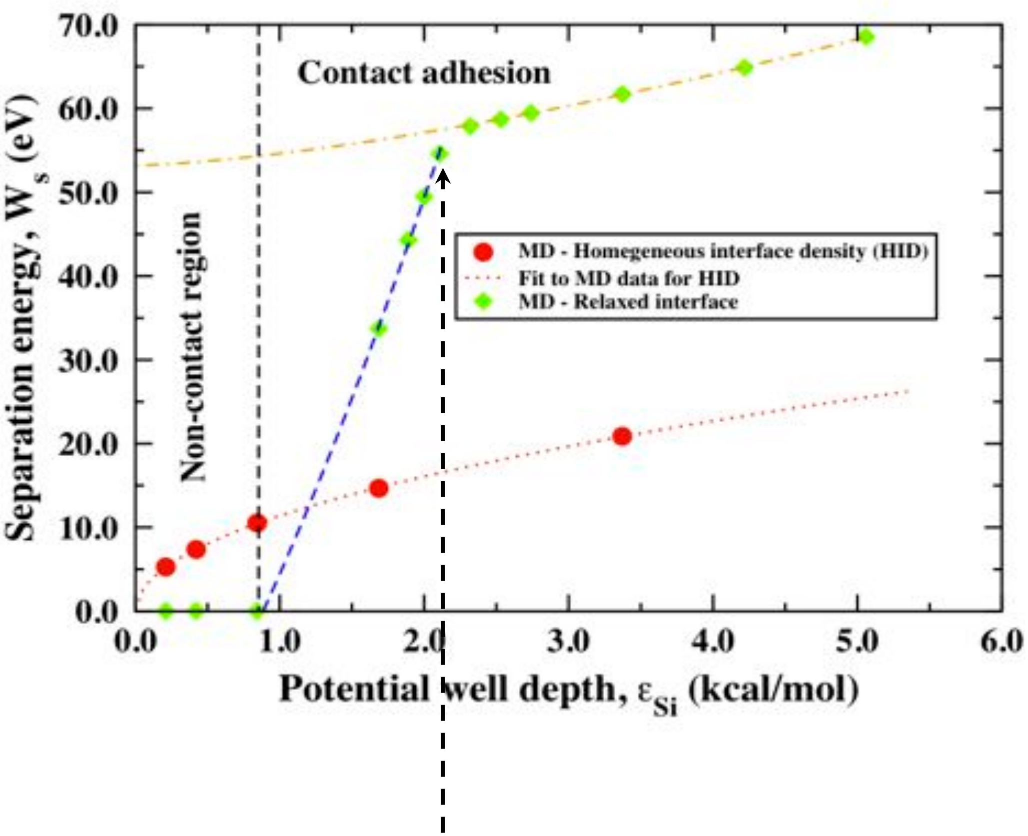
- Homogeneous a-PMB layer on silicon
- No relaxation at the interface
- Provides reference states

Void Formation Near Free Surface





Energy Regimes of *a*-PMB-Si(001) Interfaces: Adhesive Energy Transition



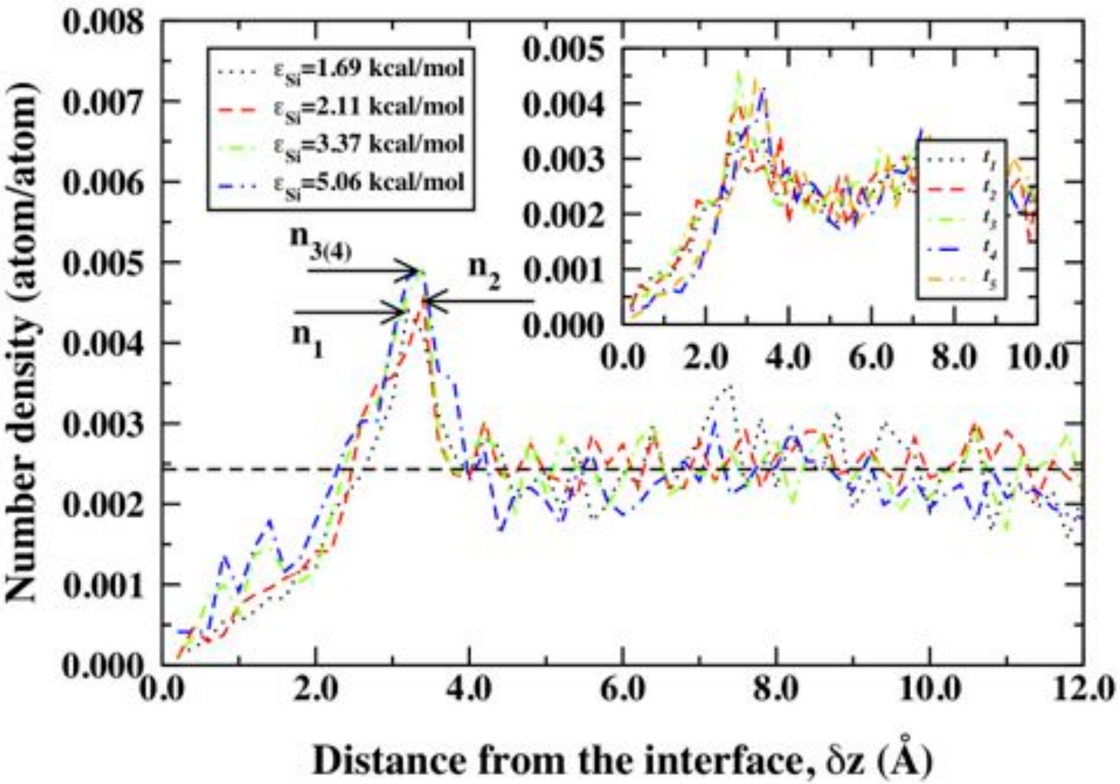
- A non-contact regime holds for small coupling strength

- The transition from non-contact to contact regime is characterized by an abrupt change in W_s, with rapid increase with coupling strength

- The rapid increase is due to density and order variations

- For large values of the coupling strength, a slow increase is observed due to density saturation, with $W_s \sim \varepsilon_{Si}^{\alpha}$, where a ≈ 0.5

Density profiles of *a*-PMB-Si(001) Interfaces

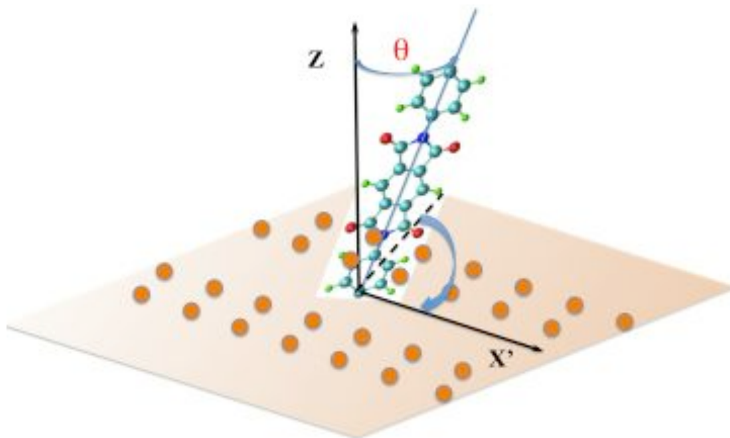


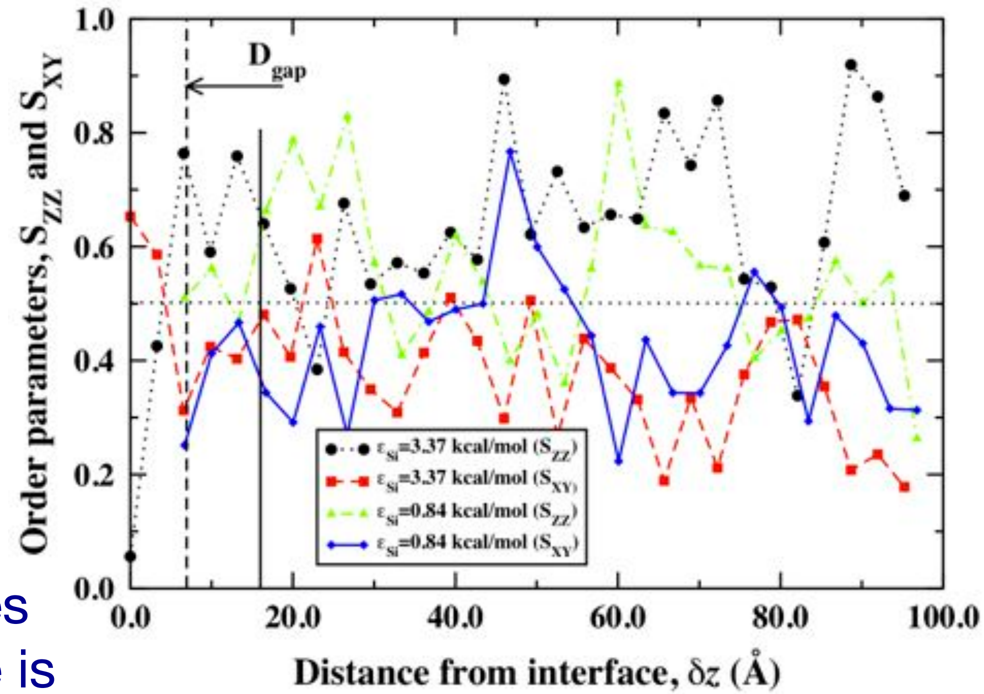
- Density profiles dynamically evolve during relaxation with non-zero coupling between adherent and substrate

- Interface relaxation (both density and ordering) largely define the adhesive behavior

Peak density grows with coupling strength (1 vs. 2) but saturates at larger couplings (3 vs. 4)

Structural Order at *a*-PMB-Si(001) Interfaces





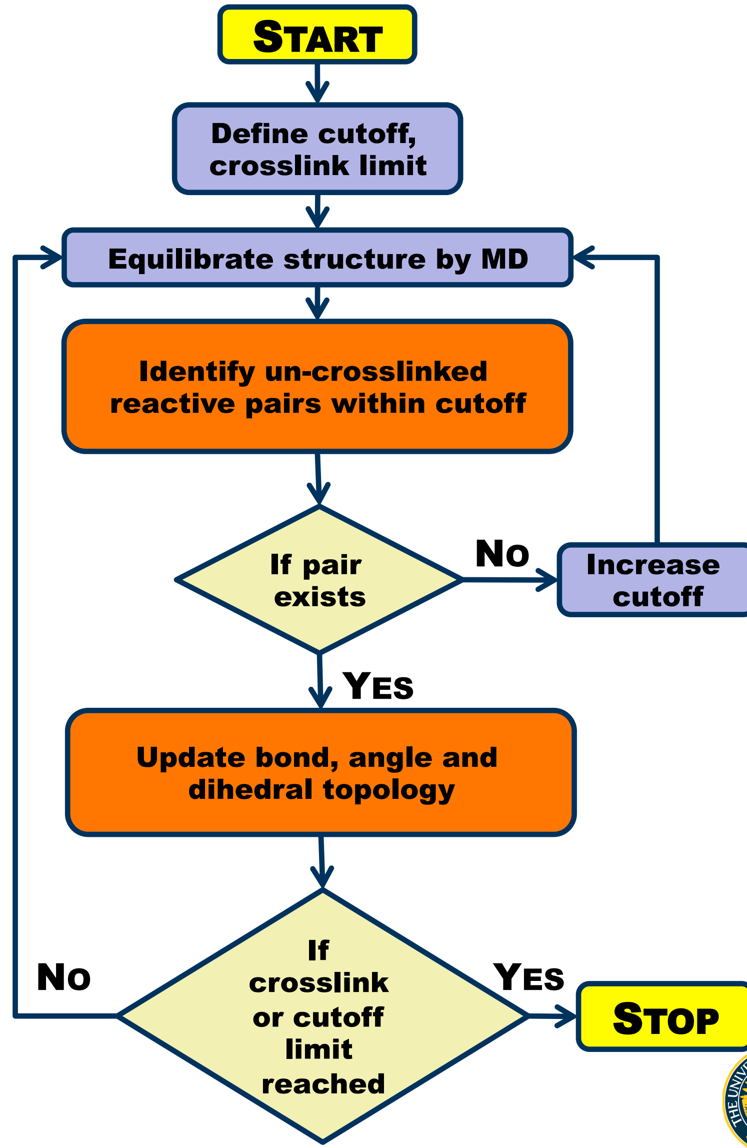
- Parallel ordering of PMB molecules with respect to the interface plane is preferred for large coupling strengths
- At the interface, the ordering along grooves formed by 2x1 surface reconstruction is favored
- Free surface acts as a repulsive wall

Order Parameter

$$S_{ua} = \frac{3}{2}\left\langle \cos(\theta)^2 \right\rangle - \frac{1}{2}$$

Polymerization Method

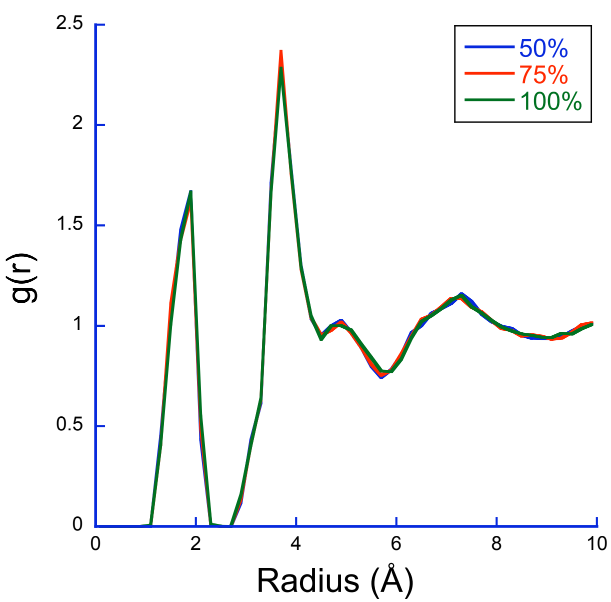
- Variation of method proposed by Varshney[1]
- More efficient than one-by-one reaction[2]
- Less stress than static/ all-at-once algorithm[2]
- Depending on cutoff, should not reach 100% cure, which is realistic

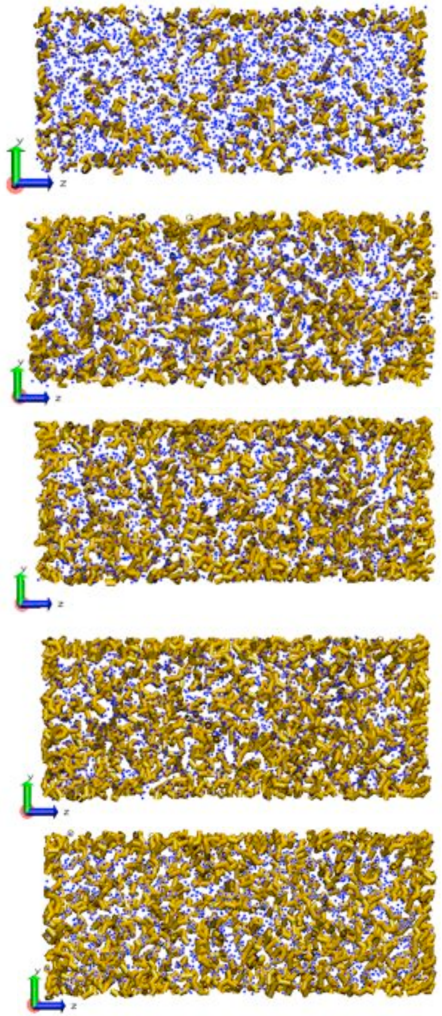


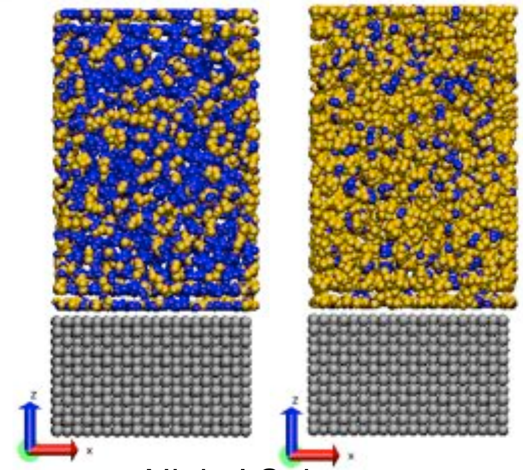
1. V. Varshney et. al., *Macromolucules*, 41 (18), 2008
2. C.K. Knox et. al, *Army Sci. Conf. Proc.* 2009

Polyethylene Bulk & Interface Structure

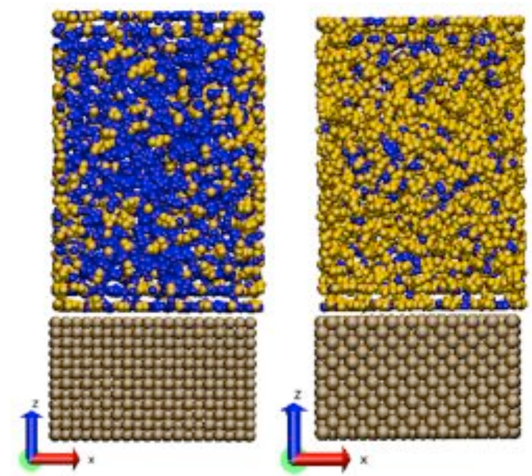
- Reaction probability has minimal effect on the final structure of polyethylene
  - Agrees with experimental study of chain growth polymers like PE and DCPD
- Maximum chain length uncorrelated with reaction probability:
  - 50%: 692;   75%: 811;   100%: 591







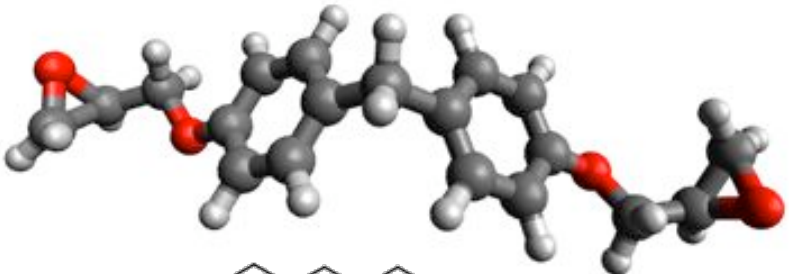
Nickel Substrate



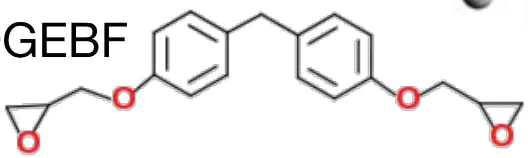
Copper Substrate; blue unreacted, yellow reacted

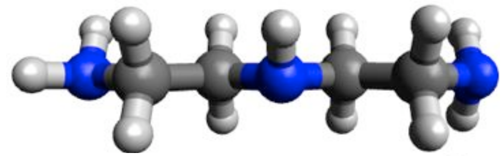
- Reaction process does not prevent layering effects

Epoxy Reaction Paths

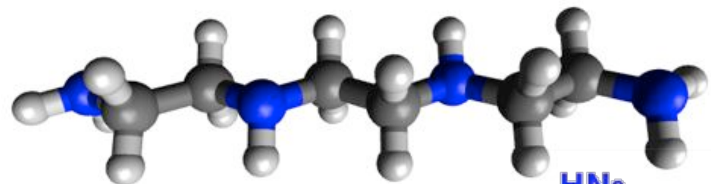


DGEBF





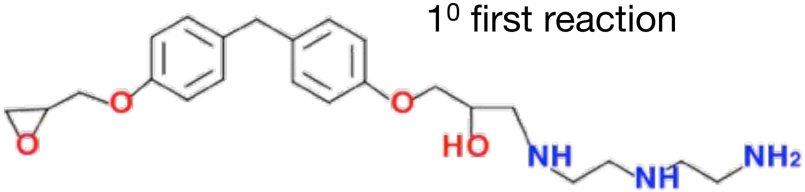
DETA

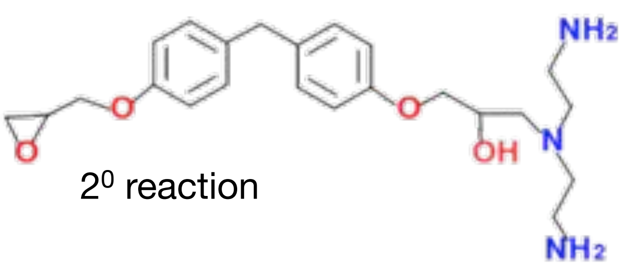


TETA

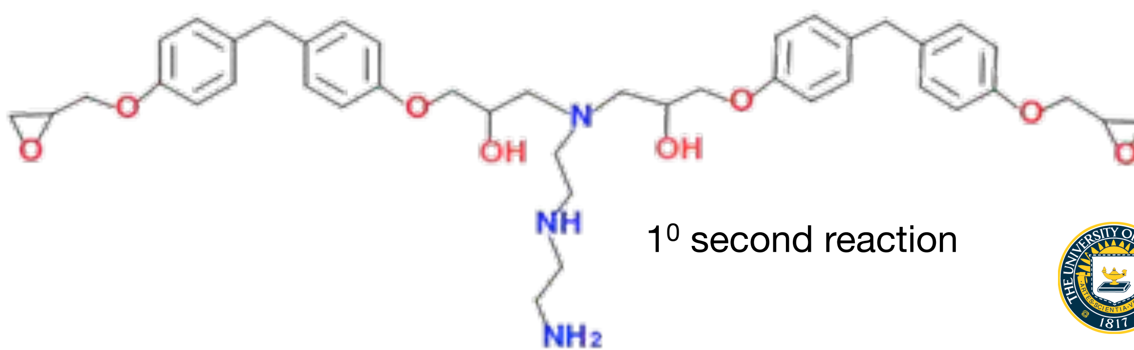
- DGEBF & DETA/TETA for hardeners
- 3 reaction pathways
  - Assumed equally reactive for a given cutoff radius
- Assumes epoxide ring activated by presence of amine group

1^0 first reaction





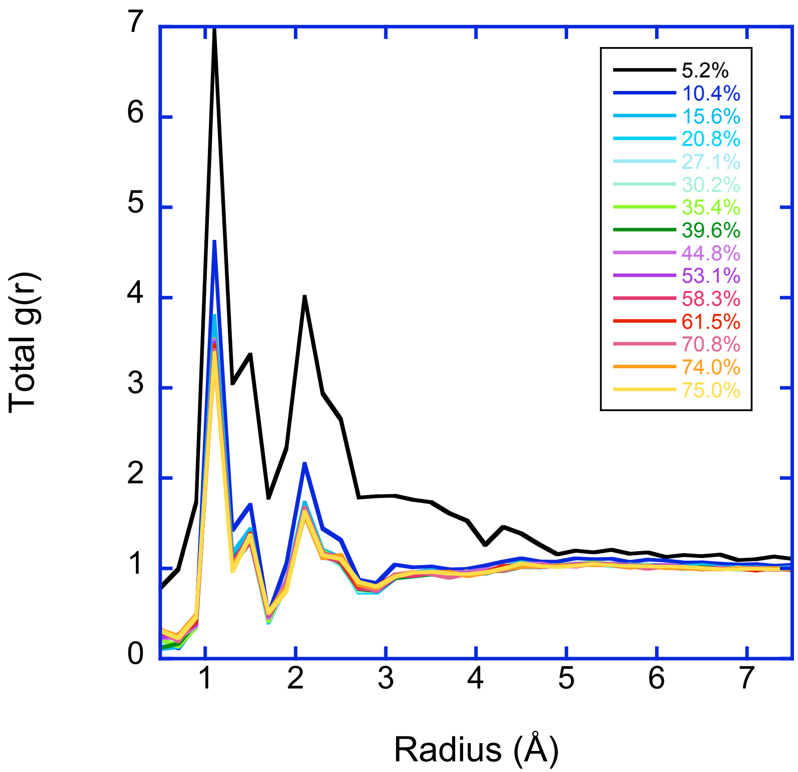
2^0 reaction



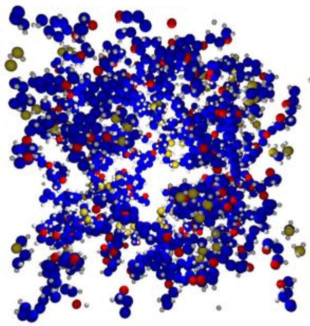
1^0 second reaction

Epoxy Cure Simulations

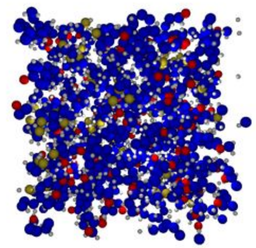
Total RDFs as a function of the degree of cure



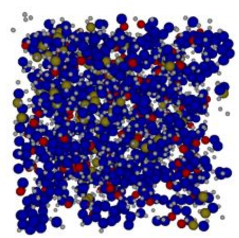
Degree of Cure



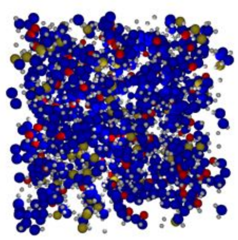
5%



26%

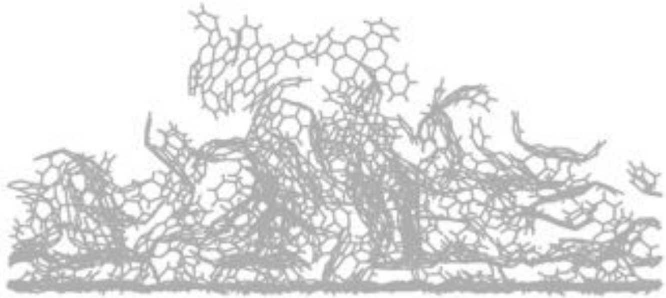


59.4%

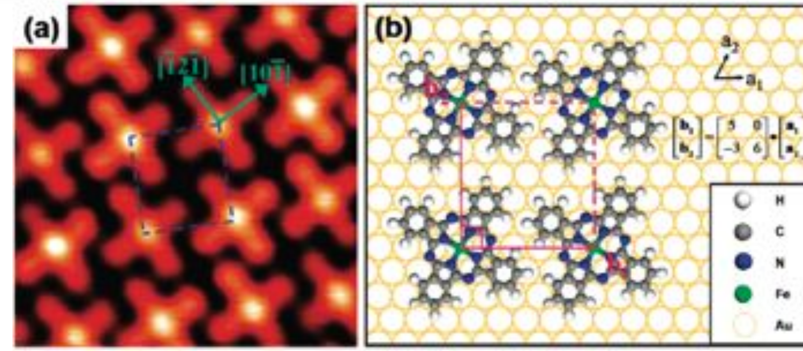


75%

Growth Behavior of CuPc

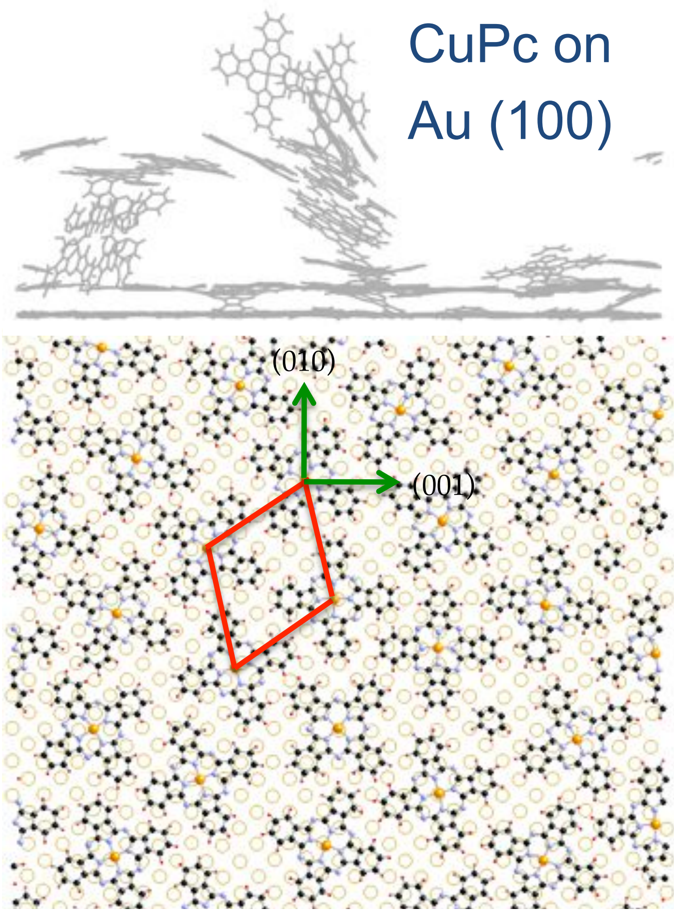


- ❖Growth behavior before force field optimization

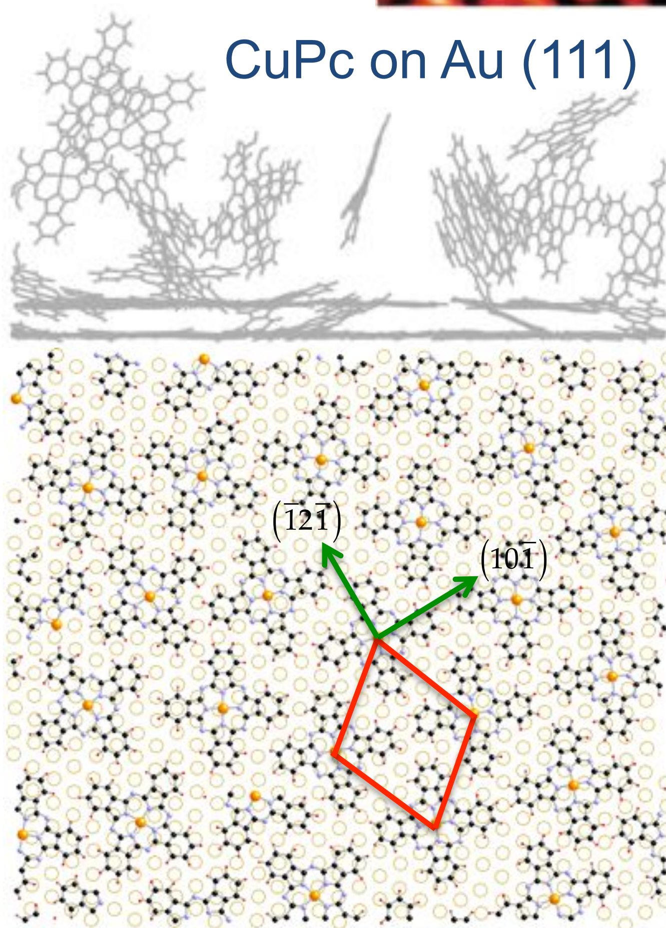


Z.H. Cheng et. al., JPC (2007)

CuPc on Au (100)



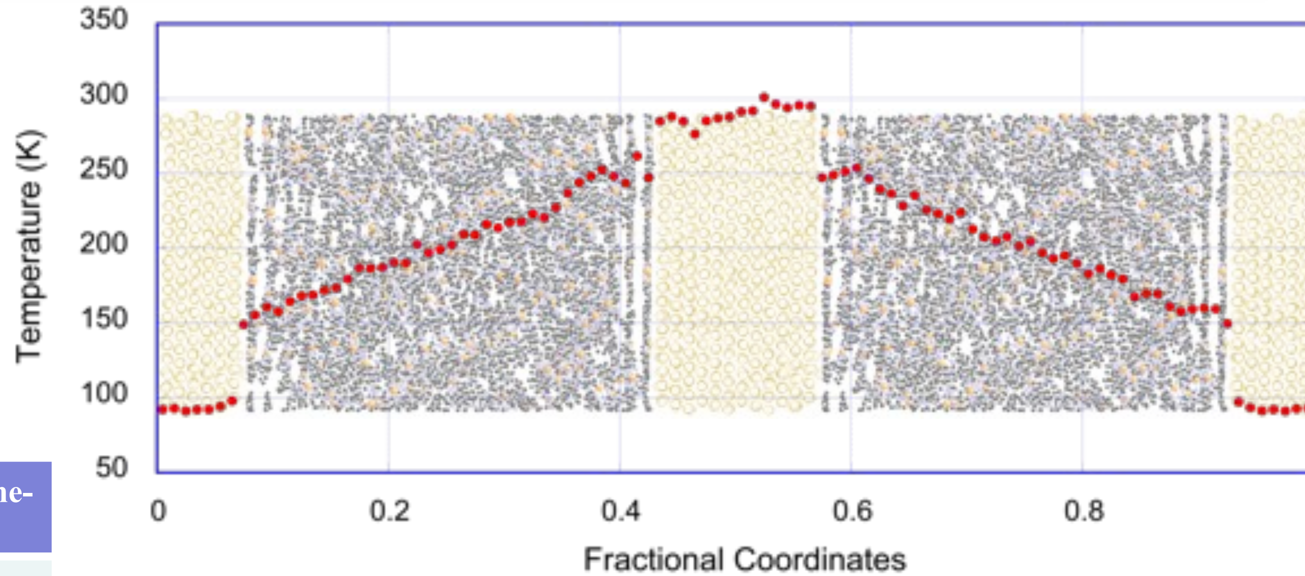
CuPc on Au (111)



- ❖Monolayer deposition of CuPc forms crystalline patterns on both (100) and (111) surfaces
- ❖This growth behavior was only observed after force field optimization

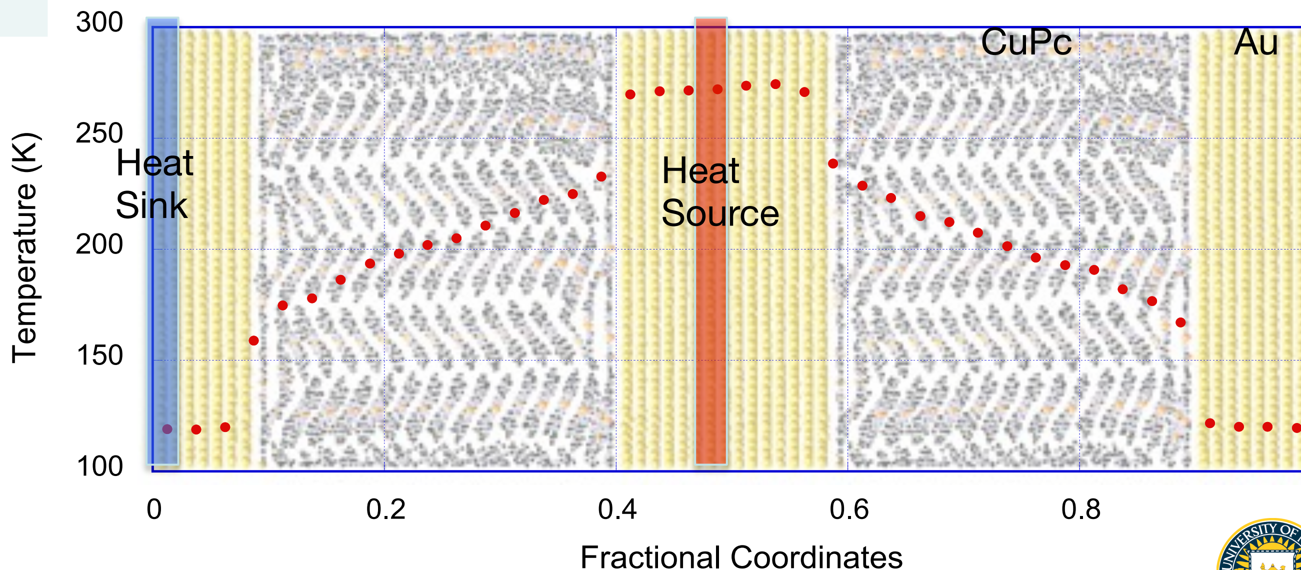
Crystalline vs. Amorphous CuPc

- CuPc molecule is deposited on Au(111)
- TBR is smaller at the amorphous-CuPc/Au than the crystalline-CuPc/Au interface

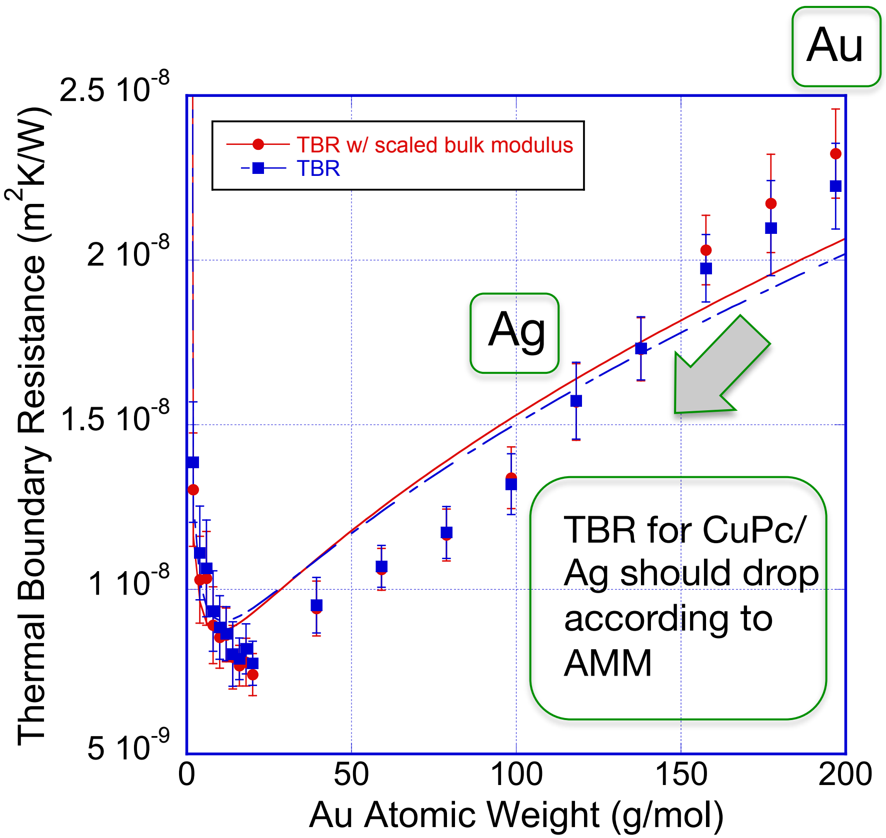


	Amorphous-CuPc/Au	Crystalline-CuPc/Au
TBR (10^{-8} m^2K/W)	1.96 ± 0.24	2.36 ± 0.20

Thermal conductivity	MD (W/mK)	Exp (W/mK)
Amorphous CuPc	0.323 ± 0.005	0.32
crystalline-CuPc	0.388 ± 0.004	0.39



Adhesion Strength vs. Acoustic Mismatch Model



Ag has a larger TBR than Au in experiments. Adhesion strength dominates!

Acoustic Mismatch Model:

$$TBR \propto \frac{1}{\tau_b} = \frac{(Z_1 + Z_2)^2}{4Z_1Z_2}$$

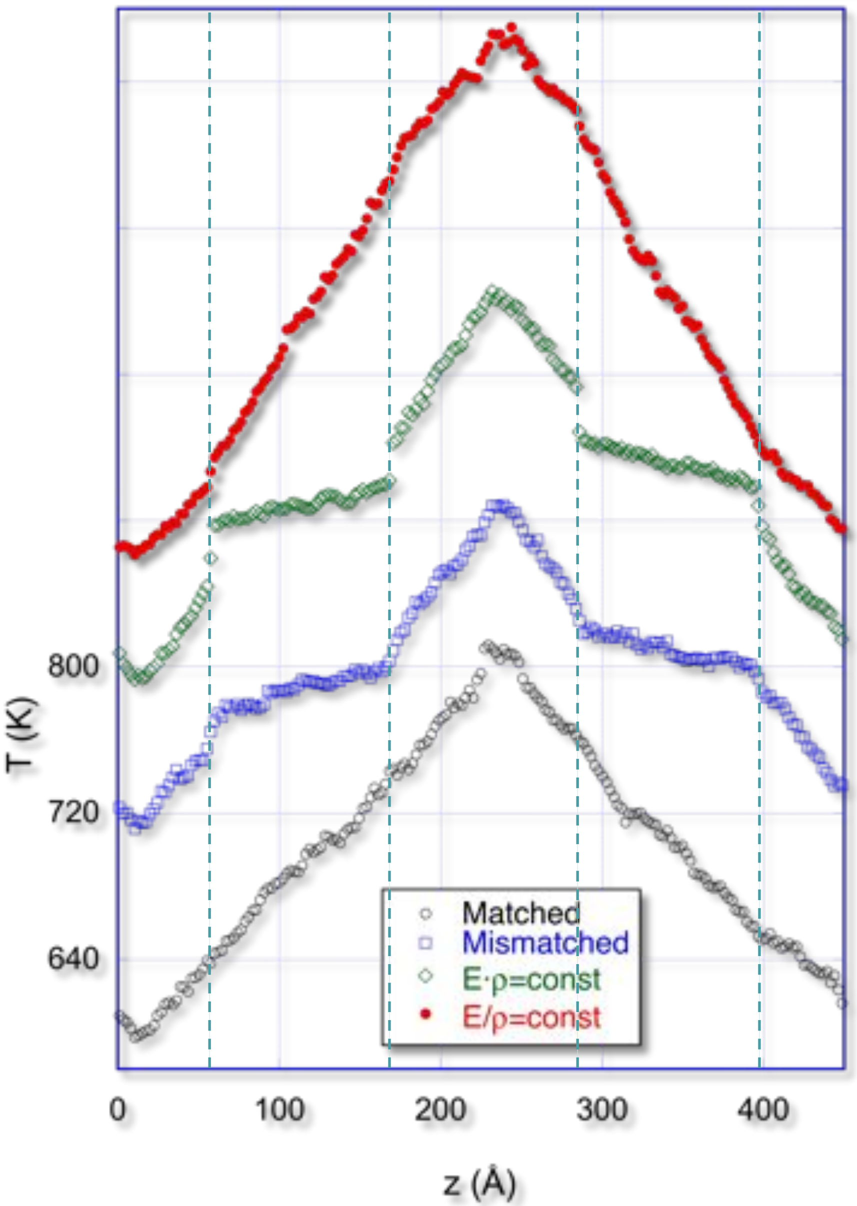
$$Z = \rho \cdot u_p = \sqrt{\rho \cdot E}$$

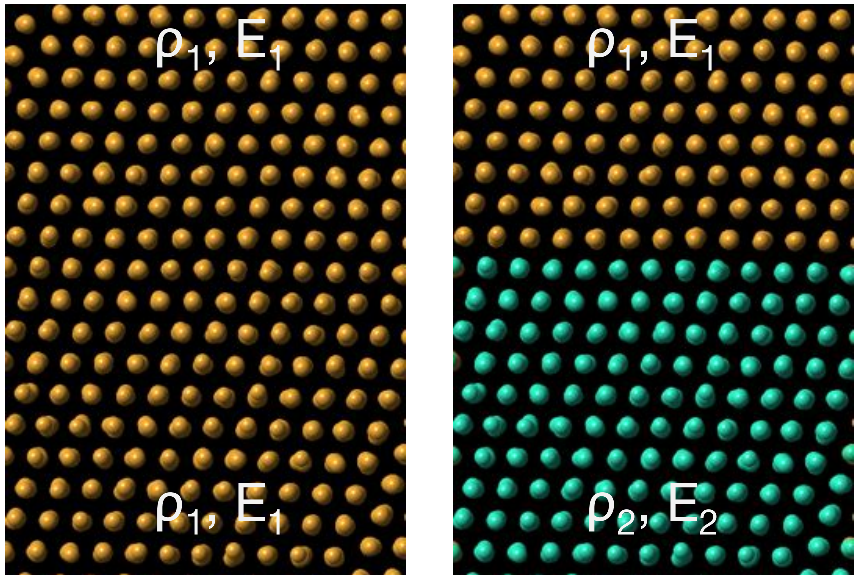
For two substrates with the bulk moduli of Ag and Au respectively, the atomic weight of the substrate is changed while keeping interactions the same.

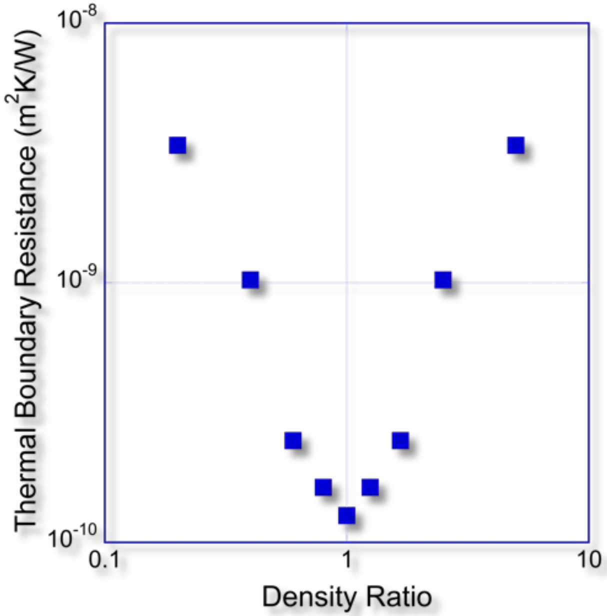
	Ag	Au
Bulk Modulus (GPa)	100	180
Lattice Constant (Å)	4.09	4.08
Atomic Weight (g/mol)	107.8682	196.97
TBR[4] (10^{-8} m^2K/W)	7.8 ± 1.6	5.4 ± 1.4

[4] Y. Jin, et al. APL **98** 093305 2011

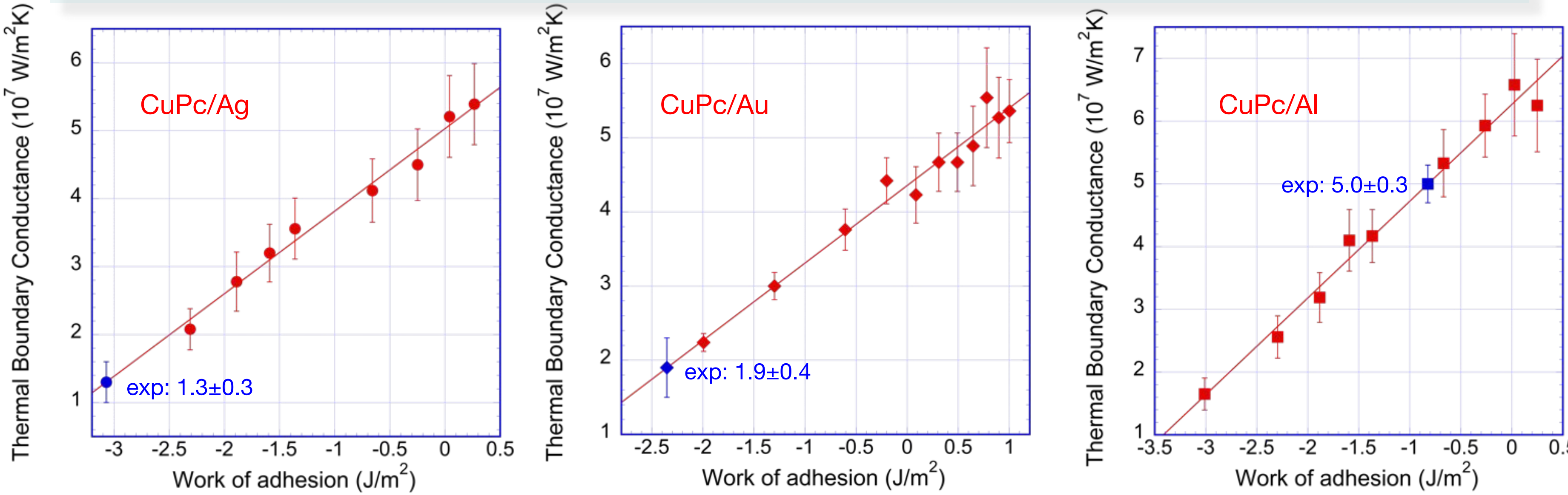
Interface in Properties Only







Adhesion Strength Dominates TBR



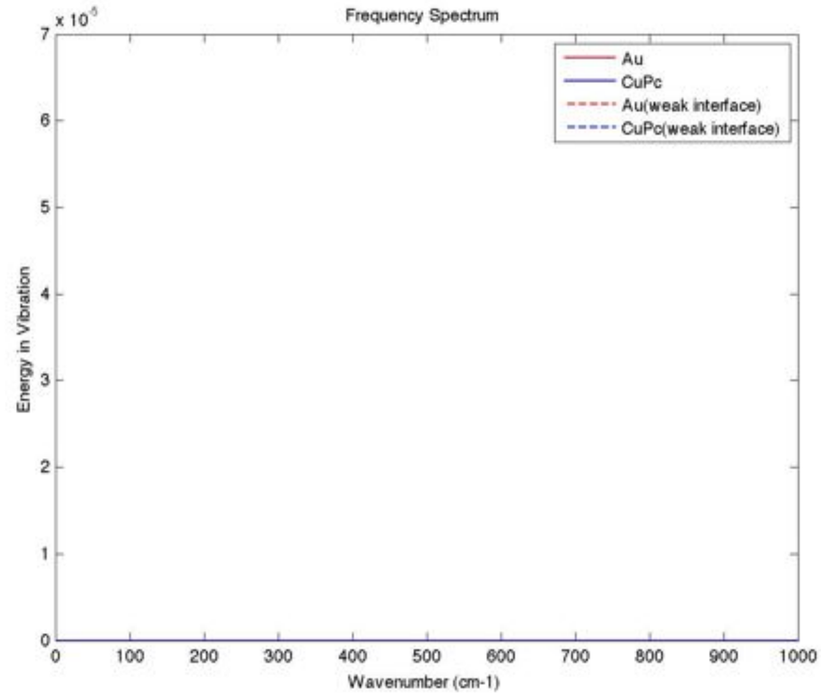
- Free surface energy for CuPc from Exp[3]: 0.035 J/m^2 and Work of adhesion for CuPc is 0.07 J/m^2
- Work of adhesion: CuPc/Al > CuPc/Au > CuPc/Ag
- The adhesion between CuPc/Au or CuPc/Ag is weaker than CuPc/CuPc[2]
- Agrees with the peel off test results from experiment[2]

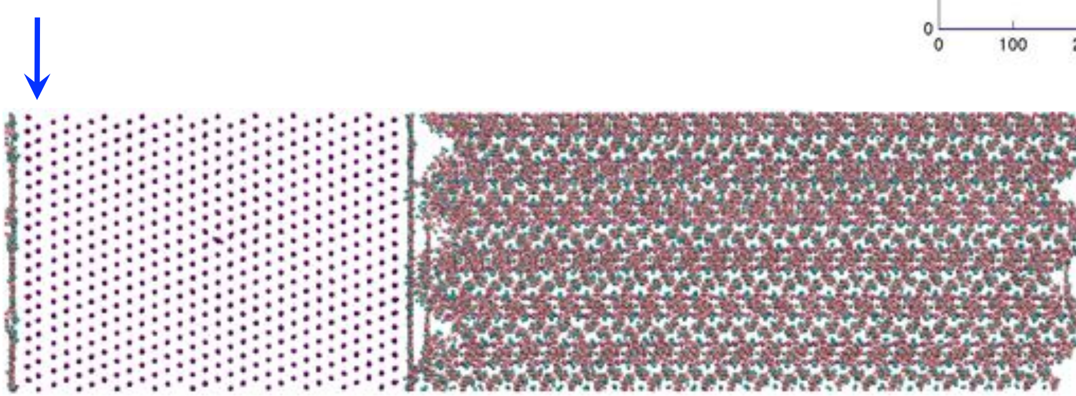
[2] Y. Jin, et al. MRS Spring Meeting 2011

[3] H. X. Wei, et al. APL **97**, 083302 2010

Phonon Coupling at CuPc/Au Interface

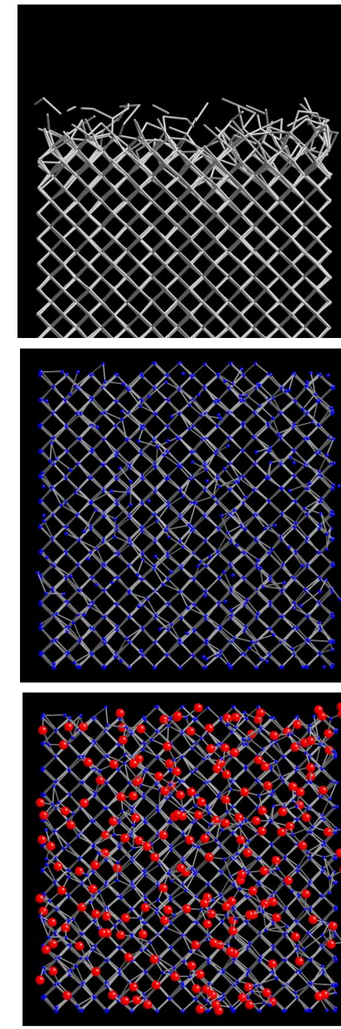
- For CuPc/Au system, 1 layer of Au atoms are perturbed
- Atomic velocity differences between perturbed and unperturbed systems are recorded to calculate phonon frequency spectrum





Summary & Outlook

- ❑ Reproduce process to generate realistic structures for property predictions and interpretation of experiments
- ❑ Findings thus far reveal:
  - ❖ Predominance of polymer layering near interfaces (staircase patterns, surface-bulk separation, surface domains, void formation)
  - ❖ Transition between contact and non-contact adhesion
  - ❖ Thermal boundary resistance (phonon velocity, mechanical impedance, structural impedance)
- ❑ Ongoing work:
  - ❖ Quantify structural signatures in materials responses
  - ❖ Thermosets
  - ❖ Interfacial modulus
  - ❖ Controlling interfacial properties



Functional molecular layers, for monitoring, sensing, or energy harvesting